

**ADVANCED DIRECT LIQUEFACTION CONCEPTS
for PETC GENERIC UNITS
Phase II**

**Quarterly Technical Progress Report
for Period April through June 1997**

by

**University of Kentucky
Center for Applied Energy Research**

CONSOL Inc.

Hydrocarbon Technologies, Inc.

LDP Associates

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ABSTRACT

Reported here are the results of Laboratory and Bench-Scale experiments and supporting technical and economic assessments conducted under DOE Contract No. DE-AC22-91PC91040 during the period April 1, 1997 to June 30, 1997. This contract is with the University of Kentucky Research Foundation which supports work with the University of Kentucky Center for Applied Energy Research, CONSOL, Inc., LDP Associates, and Hydrocarbon Technologies, Inc. This work involves the introduction into the basic two stage liquefaction process several novel concepts which includes dispersed lower-cost catalysts, coal cleaning by oil agglomeration, and distillate hydrotreating and dewaxing.

This report includes a data analysis of the ALC-2 run which was the second continuous run in which Wyodak Black Thunder coal was fed to a two kg/h bench-scale unit. One of the objectives of that run was to determine the relative activity of several Mo-based coal impregnated catalyst precursors. The precursors included ammonium heptamolybdate (100 mg Mo/kg dry coal), which was used alone as well as in combination with ferrous sulfate (1% Fe/dry coal) and nickel sulfate (50 mg Ni/kg dry coal). The fourth precursor that was tested was phosphomolybdic acid which was used at a level of 100 mg Mo/kg dry coal. Because of difficulties in effectively separating solids from the product stream, considerable variation in the feed stream occurred. Although the coal feed rate was nearly constant, the amount of recycle solvent varied which resulted in wide variations of resid, unconverted coal and mineral matter in the feed stream. Unfortunately, steady state was not achieved in any of the four conditions that were run. Earlier it was reported that Ni-Mo catalyst appeared to give the best results based upon speculative steady-state yields that were developed.

During this reporting period, after close examination of the run data, it became apparent that a simple model of the form $Ax + By \rightarrow C$ fit the data quite well where A and B are the concentrations of coal and resid in the feed and C is the total distillate product. Regression analysis was applied to data based upon feed and products in which the resid cut points were 524, 454 and 343 °C. For the 524 °C cut point, values of 0.74 and 0.39 were calculated for x and y, respectively, with an R squared value of 0.98. The corresponding values for the 454 °C cut point data were 0.63 and 0.41, respectively, with an R squared value of 0.95. No correlation was found for the 343 °C data. These data show that the activity of catalysts for producing either 524 and 454 °C- products were the same, indicating that neither Fe or Ni had any significant effect. Product distribution, however, showed that the Ni-Mo catalyst produced less 343 °C- product and more heavy distillate than the other catalysts. Based upon cost, the ammonium molybdate and the phosphomolybdic acid catalysts are preferred. Laboratory investigations have failed to provide any explanation of why the solids in the ALC-2 products could not be separated.

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SUMMARY

TASK 2.1 LABORATORY SUPPORT (UK/CAER)

Solids Separation in ALC-2

In our last Quarterly Technical Progress Report difficulties with solids separation in ALC-2, which was run at HTI during November-December, 1996, was discussed. A number of samples of process streams from that run have been separated and analyzed at the CAER. We reported that these solids laden samples could be filtered in the laboratory with Whatman #42 paper without any apparent passage of solids. This provided a number of samples that have been examined by XRD, SEM and EDS, as well as by elemental analysis. These samples were from ALC-1 and ALC-2, as well as, samples from the run made at Exxon during the fall of 1995. An anomalous result was discovered during this reporting period for a sample from ALC-2 Period 21A. It is now known that this sample does not fit the pattern for ALC-2 but rather is quite consistent with samples received for ALC-1.

SEM analyses were completed for a number of samples using magnifications up to 20,000. In all of the ALC-2 samples the particle sizes of the solids appear to be less than a few microns with the 7B sample having a greater abundance of platelets than the other two samples shown. By contrast, the Wilsonville solids are larger in size and contain a significant concentration of platelets. It has been suggested that the platelets may be related to the presence of vaterite (VT). When comparing the ALC-2 solids with the ALC-1 solids, which were successfully filtered at HTI, there isn't any dramatic difference in appearance, other than the possibility that there has been more agglomeration of the solids in ALC-1-6B. The differences in particle distribution does not suggest an obvious reason why the ALC-2 materials penetrated the solid separation media while the ALC-1 samples were all efficiently separated using the 50 micron Alstrom filter paper.

EDS analysis of the samples was completed during this reporting period. The scans of the solids samples taken from the same run were quite similar although the two runs differed. The intensity of the sulfur peak is dominant peak in the ALC-1 samples but is much reduced in the samples from ALC-2. Fe is also quite prevalent in the ALC-1 samples and much reduced in the ALC-2 while Ca is the dominant peak in the ALC-2 samples. It appears that the intensity of the sulfur peak is related to the concentration of the added Fe and is little affected by the Fe present in the mineral component of the coal. The scans of the Wilsonville samples shows a higher sulfur peak than for the ALC-2 samples but somewhat smaller than for the ALC-1 samples. This increased sulfur peak would be related to the sizable amount of Fe that was added in these runs.

XRD patterns were obtained for a number of solids during this period. The ALC-2 solids are quite uniform with quartz being the dominant peak. Significant quantities of VT are observed in two of the samples. Pyrrhotite (PY) is quite prevalent in 7B but is significantly reduced in 18A and 21B, the latter being quite small. Apparently the PY in 7B must be related to the fresh Fe addition. For the ALC-1 samples, large amounts of quartz, PY and anhydrite (AN) are present. Even though a large portion of the Ca was removed during the low-pH oil agglomeration in ALC-1, AN was still a major component of the crystalline material in the solids. For the Wilsonville solids, quartz is the dominant peak with significant quantities of both VT and PY being present. Kaolinite was also present in the sample from Run 258K. Since higher sulfur and PY concentrations parallel higher added Fe concentrations, the addition of Fe may have a beneficial effect on separation of solids

through formation of PY. This has not been verified and the mechanism by which PY formation could facilitate solids separation is difficult to understand.

Data Analysis of ALC-2 Results

In our previous quarterly progress report, Ni-Mo was suggested as being the more active catalyst for resid conversion in ALC-2. This was based primarily on the wide variation in resid conversions that varied from 79.8 to 90.3 wt% of maf coal. Coal conversion was almost the same for all four of the catalysts ($95.0 \pm 0.66\%$). In the run the composition of the feed stream differed quite substantially.

Since the coal feed rate remained relatively constant, the variation was in the composition of the recycle stream due to changes in the solids and the 524 °C+ resid concentrations. Since resid conversion is affected by concentrations of resid and IOM in the feed, these values could be misleading. Eliminating IOM from this calculation increases the resid conversion values but the relative order and differences between the values remain the same. A simple model was tested that represents the conversion of coal and resid to distillable material, each at their own rate, as represented by the following equation.

$$[Reactive\ Coal] x + [Resid] y = [Product]$$

Using regression analysis, the values of x and y that gave the best fit to the proposed model was determined. Using cut points of either 524 °C or 454 °C, values of x and y were obtained that had R^2 values of 0.98 and 0.95, respectively. When the reference data from ALC-1-1 was included, the fit of the data diminished significantly for both cut points. For a 343 °C cut point feed and product compositions, no linear correlation exists. These results lead to the conclusion that the activities for both 524 and 454 °C conversion for each of the four catalysts in ALC-2 were the same. The lower yield of 343 °C- product and higher 343 to 524 °C product for the Ni-Mo catalyst indicates that addition of Ni has a detrimental effect on the product distribution.

Catalyst Studies

The liquefaction activity of particulate MoS_2 was evaluated during this reporting period. This catalyst was prepared by two different methods from molybdenum trisulfide, which was prepared by acidifying an aqueous solution of ammonium tetrathiomolybdate with formic acid. In one case the disulfide was prepared from a slurry of the trisulfide in tetrahydrofuran which was heated at 450 °C in a microautoclave in H_2 to give a material having a surface area of 38 m²/g. The disulfide was also prepared by rapidly heating MoS_3 to 450 °C in flowing H_2 . The resulting surface areas ranged from 27-33 m²/g. Ammonium dioxymolybdate was also prepared and evaluated. Both MoS_3 and MoS_2 particulate catalysts exhibit improved coal conversion compared to the thermal reaction. The increase in conversion with MoS_3 (13%) was higher than that of MoS_2 (8%) which parallel the increase in surface area. However, the resid conversions with both of the sulfides showed no improvement over the thermal reaction. By contrast, both coal conversion and resid conversion increased for coal impregnated with AHM or AOTM at the same level of Mo loading, which indicates that both the catalyst dispersion and the nature of the active phase present during the reaction are important for coal liquefaction.

TASK 2.1 LABORATORY SUPPORT (CONSOL)

Results from analysis of ALC-2 samples were reported. No unusual properties of the coal or oil

were found that would explain difficulties encountered with the solids separation step. Process oil properties were consistent for the entire run suggesting that the choice of catalyst system had little impact. The first-stage SOH oils and the RPSOH oils had very high phenolic-OH concentrations (approximately 25%) which were completely removed after hydrotreating.

TASK 4 CONCEPTUAL PROCESS DESIGN

TASK 4.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

Analysis of the ALC-2 run data continued. Solids accumulation was larger than expected with accumulation continuing until the ninth day of operation. The total accumulated was two to three times more than expected. The effect of recycling RPSOH was to dramatically decrease the yield of RPSOH. RPSOH was recycled due to problems with the solids separation equipment. An analysis of the H₂S product stream indicated that the addition rate was much higher than targeted. An analysis of the solids in the recycle stream suggested that a considerable amount of Fe was being recirculated unless the Fe measurement in the feed coal was incorrect. However, many measurements were made of the Fe in the feed coal during preparation of the impregnated coals. A review of Sandia's proposed donor solvent hydrotreating test program was conducted.

SECTION ONE

**UNIVERSITY OF KENTUCKY
CENTER FOR APPLIED ENERGY RESEARCH**

Work Performed

TASK 2.1 LABORATORY SUPPORT (UK/CAER)

Solids Separation in ALC-2

In ALC-2, which was run at HTI during November-December, 1996, separation of solids by either toluene extraction of the CVSB or filtration of the O-6 bottoms failed due to penetration of solids through the separation media. When toluene extraction was being used, solids were being carried over in the TEO which was being recycled to the unit. At the same time, quinoline insolubles in the TES were low indicating that quinoline soluble material was being rejected with the solids. The latter were less a problem of the solids separation media but rather the volume of CVSB feed to the toluene extraction unit. A complete description of the solid separations that were used in the run is described in the previous Quarterly Technical Progress Report.¹

Laboratory filtration has been used as a method for investigating the properties of various solids containing samples that were generated in ALC-2 as well as samples from ALC-1 and Wilsonville. Samples of O-6 bottoms from periods 7B, 18A and 21B were slurried in toluene in a 6/1 wt/wt ratio and filtered through a series of papers starting with Whatman #41 followed by Whatman #42 and subsequently Millipore 0.45 μ m paper. Ash analysis of the filtrates indicated that solids did not pass through the Whatman #42 paper although a sizable amount did pass through the Whatman #41 paper. Comparable filtrations were also done on ALC-1 samples for all of the balance periods. Results from analysis of these materials were reported previously, including the optical microscopic results which showed the ALC-1, ALC-2 and Exxon samples were all very similar and quite uniform in size. Since the optical technique failed to provide any explanation as to why ALC-2 could not be filtered, a more thorough examination by SEM was undertaken.

Previously we reported that the sulfur content of the ALC-2 Period 21A sample that we received from HTI was significantly higher than for the 7B or 18A samples. This high sulfur content in the 21A sample was also inconsistent with the sulfur content of the CVSB Period 21 sample. More recently, a sample of ALC-2 Period 21B CVSB that was received from HTI was subjected to solids separation and analyzed. The elemental analysis results and the various instrumental analysis techniques applied to these two samples show that the 21A sample must be mislabeled and not taken from ALC-2. It is much more consistent with the solids generated in ALC-1, as will be shown below.

Scanning Electron Microscopy (SEM) Scans of Solids SEM analyses were completed during this reporting period of solids from ALC-1 (see Figure 1), ALC-2 (see Figure 2), and Wilsonville (see Figure 3). Although scans were made at magnifications up to 20,000x, the figures include only 5000x magnification scans. The particle sizes of the ALC-2 solids appear to be less than a few microns with the 7B sample having a greater abundance of platelets than the other two samples shown. By contrast, the Wilsonville solids are significantly larger in size. Whether the size has been affected by the ROSE SR process used at Wilsonville or the longer reaction time at HTI isn't known. When comparing the ALC-2 solids with the ALC-1 solids, which were successfully filtered at HTI, there is no dramatic difference, other than the possibility that there has been more agglomeration of the solids in ALC-1-6B. Overall, for most of these ALC samples, the particle sizes are all quite

small with an abundance of particles smaller than 1 micron and very few particles larger than 2-3 microns, except for the ALC-1-6B sample already noted. Certainly the differences in particle distribution does not suggest an obvious reason why the ALC-2 materials penetrated the solid separation media while the ALC-1 samples were all efficiently separated using the 50 micron Alstrom filter paper.

Chemical Analysis (EDS) of Solids Energy dispersive spectroscopy was completed this reporting period on samples of solids from ALC-1 (see Figure 4), ALC-2 (see Figure 5), and Wilsonville (see Figure 6). Note that in a number of the figures the sulfur peak was labeled Mo because the energy levels of the x-ray emissions from these two elements are nearly the same. The scans are quite similar for the PFC samples from ALC-1 shown in Figure 4 which were taken during the five different balance periods. The intensity of the sulfur peak, which is the dominant peak in each of these samples, varies relative to the Si and Al peaks. Fe is quite prevalent in each of the samples. The ALC-2 samples shown in Figure 5 are quite uniform among themselves but still very different from the ALC-1 samples. Ca is apparently the dominant peak in each of the samples with the sulfur peak being much smaller. The corresponding intensities of the Si and Al peaks also increase sharply while the Fe peak is quite small. The latter are true even in the 7B sample which was taken when Fe was being added at a rate of 0.18 wt% on dry coal.

The EDS scans of the Wilsonville samples in Figure 6 show a sulfur content less than in the ALC-1 samples but certainly more than for the ALC-2 samples. The dominant peaks in these two samples are either Ca, for the sample from Run 258K, or Si, in the sample from Run 262. The Fe peaks appear to be slightly higher than for the ALC-1 samples and much higher than for the ALC-2 samples. The differences between these samples are the smaller sulfur peaks in the ALC-2 samples.

X-ray Diffraction XRD patterns were obtained for a number of samples of solids from ALC-1 (see Figure 7), ALC-2 (see Figure 8), and Wilsonville (see Figure 9) during this reporting period. The solids from Periods 7B, 18A, and 21B, shown in Figure 8, are quite uniform with the quartz being the dominant peak. Significant quantities of vaterite (VT) are observed in the 7B and 18A samples with the quantity significantly reduced in the 21B sample. Pyrrhotite (PY) at 2 theta positions of 34 and 44 is quite prevalent in 7B but is significantly reduced in 18A and 21B, the latter being quite small. Apparently the PY in 7B must be related to the fresh Fe addition. In the previous quarterly report, an XRD scan of a sample labeled 21A241 was presented which showed very large amounts of PY and AN, which are inconsistent with the ALC-2 samples. Apparently the sample that was received at the CAER was not labeled correctly.

For comparison, samples of pressure filter cakes (PFC) from each of the balance periods in ALC-1 were available for examination. Each sample was extracted with THF to remove any toluene insolubles that were present. The XRD patterns, shown in Figure 7 indicate large amounts of quartz (QZ), PY and AN being present. The AN was quite significant in all the samples except for 25B. Originally, it was thought that anhydrite formed when the coals were low-pH oil agglomerated, however, the coal run during 6B was untreated. Even though in ALC-1 a large portion of the Ca was removed during the low-pH oil agglomeration, anhydrite was still a major component of the crystalline material in the solids. Pyrrhotite was also quite significant since a large amount of Fe (1 wt% on dry coal) was added as catalyst during the run.

The XRD patterns of the Wilsonville solids are quite similar. These solids were produced while BT Wyodak coal was being run and Fe₂O₃ was being added as catalyst. Quartz is the dominant peak with significant quantities of both VT and PY being present. KA was also present in the sample from Run 258K. It appears from these comparisons that the presence of PY in the samples is related to fresh Fe addition and not mineral Fe addition, since only in ALC-2 Periods 18A and 21B were the PY peaks either quite small or absent. This is somewhat surprising because of the significant amount of Fe that was present in these samples that were introduced in the mineral content of the feed coal. Since higher sulfur and pyrrhotite concentrations parallel higher added Fe concentrations, the addition of Fe may have a beneficial effect on separation of solids through formation of pyrrhotite. This has not been verified and the mechanism by which PY formation could facilitate solids separation is difficult to understand.

Data Analysis of ALC-2 Results

Results from ALC-2 have suggested that the Ni-Mo catalyst tested during Condition #3 was more active for resid conversion than Mo or the Mo-Fe combination. Resid conversions, however, differed significantly, varying from 79.8 to 90.3 wt% of maf coal.² Coal conversion, on the other hand, i.e., conversion to quinoline soluble product, was almost the same for all four of the catalysts (95.0±0.66%). In the run the composition of the feed stream differed quite markedly. However, the coal feed rate remained relatively constant throughout the run, especially during the balance periods.³ The major difference was in the composition of the recycle stream.⁴ This is shown graphically in Figure 10 where both the solids and the 524 °C+ resid are shown to vary quite significantly. The IOM component of the solids was actually 1.4 times greater in Condition #3 than in Condition #1. The resid conversion equation addresses conversion of resid and feed coal as well as the IOM that was recycled in the process solvent as shown in Equation 1.

$$Resid\ Conv = 100 * \frac{[Coal+Resid+IOM]_{Feed} - [IOM+Resid]_{Product}}{[Coal]_{Feed}} \quad Eq.1$$

Since the IOM in the recycle solvent varied quite significantly during the run that will impact the resulting resid conversion numbers. Because the IOM that is initially generated from the coal during its first pass does not likely further convert to any extent, the resid conversion values were examined by removing IOM from the terms for feed and product in the calculation of resid conversion in Equation 2.

$$[Resid\ Conv]_{IOM\ Free} = 100 * \frac{[Coal+Resid]_{Feed} - [Resid]_{Product}}{[Coal]_{Feed}} \quad Eq.2$$

The values shown in Table 1 show that although the absolute values for resid conversion change, the adjustment does not affect the order of the values.

Equation 3 represents the conversion of coal and resid to distillable material, each at their own rate.

$$[Reactive\ Coal] x + [Resid] y = [Product] \quad Eq.3$$

In this case, reactive coal is the amount of coal that becomes soluble in quinoline. Using regression analysis, the values of x and y were determined for two different cut points. Using cut points of either 524 °C gives values of x and y which have an R² value of 0.98 indicating a very good fit of the data. For a cut point of 454 °C, the fit of the data decreased giving an R² value of 0.95. When the reference data from ALC-1-1 was included, the fit of the data decreased for both cut points indicating a poorer fit of the data. For a 343 °C cut point feed and product compositions, which are shown in Figure 11, no linear correlation following Equation 3 exists.

	Cut Point	x	y	R ²
ALC-2	524 °C	0.74	0.39	0.98
ALC-2	454 °C	0.63	0.41	0.95
ALC-2 + ALC-1-1	524 °C	0.84	0.25	0.89
ALC-2 + ALC-1-1	454 °C	0.62	0.44	0.81

For all the catalysts used in ALC-2 for a 524 °C cut point, 74% of the reactive coal was converted to distillate product along with 39% of the resid. The corresponding values for producing 454 °C-product are 63% and 41%, respectively. Even though there was significant variation in the feed composition, catalysts were essentially equivalent for when cutting the products at either 524 or 454 °C. This was not true for producing 343 °C- product, which indicates wide varying properties of the catalysts for producing light distillates. As shown in Figure 11, the Ni-Mo catalyst use in Period #17 produced less distillate than the other catalysts. Therefore, it appears that addition of Ni has a detrimental effect on the product distribution.

Liquefaction Activity of Particulate MoS₂

Molybdenum sulfide has been evaluated as a lowcost catalyst for direct liquefaction. One approach is to exfoliate molybdenite to generate high surface area catalysts.⁵ Another approach has been to prepare high surface area MoS₂ by thermally decomposing ammonium tetrathiomolybdate or molybdenum trisulfide.⁶ Molybdenum trisulfide was prepared by acidifying an aqueous solution of ammonium tetrathiomolybdate with formic acid.⁶ Elemental analyses calculated for MoS₃: Mo, 49.9%. Found: Mo, 49.8%.

Molybdenum disulfide was prepared from a slurry of the trisulfide in tetrahydrofuran which was heated at 450 °C in a microautoclave in H₂ (7.0 MPa at ambient temperature) for 15 min. The resulting material had a surface area of 38 m²/g and showed low intensity bands in the XRD indicating low crystallinity. The XRD pattern was consistent with the pattern reported previously for MoS₂.⁷ Molybdenum disulfide was also prepared by rapidly heating MoS₃ to 450 °C in flowing H₂ (20 to 100 cc/min) at ambient pressure and holding for 0.5 to 2 hrs.⁸ The reduction conditions and resulting surface areas are summarized in Table 2. The resulting surface areas are all lower than the starting trisulfide. The surface areas of the disulfides ranged from 27-33 m²/g and the XRD scans indicated the materials were amorphous.

Ammonium dioxodithiomolybdate was prepared by treating ammonium heptamolybdate in excess

ammonium hydroxide solution with H_2S .⁹ The reaction temperature was held at approximately 5 °C during the H_2S addition. The dioxodithiomolybdate salt is quite unstable in aqueous solution.¹⁰ We found that in aqueous solution the intensity of both the 321 and 393 nm bands in the ultraviolet region decreased in intensity by 20% in 4 hours at ambient temperature. By $^{95}\text{MoNMR}$ we found that 75% of the AOTM had decomposed within 24 hours which substantiates the observations made by Lutz et al.¹¹ Since AOTM is stable in methanol,¹² it was impregnated on coal from a methanol solution after which the solvent was removed by evaporation.

The coal liquefaction results using these particulate molybdenum sulfides are compared with AHM and AOTM impregnated coals as shown in Table 3. Liquefaction experiments were run at 440 °C in 50 ml microautoclaves for 30 min. The reactants, including 3 g dry coal, 1.8 g heavy distillate and 3.6 g deashed resid, were added to the reactor which was then pressurized to 7.0 MPa at ambient temperature. The run conditions and product workup procedures have been described in previous reports.

Both MoS_3 and MoS_2 particulate materials exhibit improved coal conversion compared to the thermal reaction. The increase in conversion with MoS_3 (13%) was higher than that of MoS_2 (8%) which parallel the increase in surface area. However, the resid conversions with both of the sulfides showed no improvement over the thermal reaction. By contrast, both coal conversion and resid conversion increased for coal impregnated with AHM or AOTM at the same level of Mo loading. This indicates that both the catalyst dispersion and the nature of the active phase present during the reaction are important for coal liquefaction.

References

1. Advanced Direct Liquefaction Concepts, Quarterly Technical Progress Report, DOE/PC/91040-80. May 1997.
2. See Table 8, page 2-24 in reference 1.
3. See Figure 6, page 2-43 in reference 1.
4. See Table 7, page 2-23 in reference 1.
5. Bockrath, B.; Parfitt, D.; Miller, R.; Keller, M.; Bittner, E. Dispersed Catalysts for Co-processing and Coal Liquefaction. Proceedings of the U. S. Department of Energy Coal Liquefaction and Gas Conversion Contractors Review Conference. Pittsburgh, PA. August 29-31, 1995. p 629; Bockrath, B. C.; Parfitt, D. S. *Catalysis Letters* 19956, 33, 201.
6. Eggerston, F. T.; Roberts, R. M. *J. Phys. Chem.* **1959**, 63, 1981; Cugini, A. V.; Martello, D. V.; Krastman, D.; Baltrus, J. P.; Ciocco, M. V.; Frommell, E. F.; Holder, G. D. *Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1995, 40(2), 370.
7. Wickman; Smith; *Am. Mineral.* 1970, 55, 1843. See JCPDS-ICDD Database File 24-0513.
8. Wildervanck, J. C.; Jellinek, F. "Crystallinity of Molybdenum and Tungsten Sulfides", *Zeitschrift für anorganische and allgemeine Chemie.* 1964, vol 328, 309.
9. McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. "Syntheses and characterization of Ammonium and Tetraalkylammonium thiomolybdates and thiotungstates", *Inorganica Chimica Acta* 1983, 72, p 205-210.

10. Harmer, M. A.; Sykes, A. G. "Kinetics of the interconversion of sulfido- and oxomolybdate (VI) species $\text{MoO}_x\text{S}_{4-x}^{2-}$ in aqueous solutions", Inorg. Chem. 1980, 19, 2881-2885.
11. Lutz, O.; Nolle, A.; Kroneck, P. Z. Naturforsch. 1977, 32a, 505-506.
12. Muller, A.; Krickemeyer, E. Inorganic Synthesis 1990, 27, 47-51 (see sect. B on page 48-49).

Table 1. Resid Conversion Values for ALC-2		
Period	Standard	Values without IOM
#7	84.6	90.7
#12	79.8	84.6
#17	90.3	95.2
#21	83.3	87.6
#6 in ALC-1	90.6	95.7

Table 2. Surface Area of MoS ₂ Prepared from Reduction of MoS ₃ at 450 °C			
Sample	H ₂ flow rate (ml/min)	Reduction time (Hrs)	Surface area (m ² /g)
MoS ₃	--	--	47.7
MoS ₂ - No. 1	100	2	31.3
MoS ₂ - No. 2	20	0.5	27.0
MoS ₂ - No. 3	20	2	32.9

Table 3. Comparison of MoS ₃ and MoS ₂ particulate catalysts with impregnated Mo catalysts					
	Catalysts				
	none	MoS ₃	MoS ₂ - No. 1	AHM impregnated ^a	AOTM impregnated ^b
moisture in coal, wt%	8.9	8.9	8.9	0	0
Mo conc, mg/kg dry coal	0	200	200	200	200
H ₂ S, wt% dry coal	5.6	5.6	5.6	5.6	5.3
HC gases, wt% dry coal	6.5	8.3	11.0	8.1	8.4
CO _x gases, wt% dry coal	7.4	7.7	8.6	7.4	8.1
524 °C+ resid conv., wt% maf coal	55.3	55.8	54.8	67.1	72.0
THF Conversion, %	60.7	73.6	68.5	89.9	92.5
a. Coal impregnated with aqueous AHM solution and then dried. b. Coal impregnated with methanolic AOTM solution and dried to remove solvent.					

Figure 1
SEM Scans of ALC-1 Solids
Periods 6B, 13B, 17B and 25B

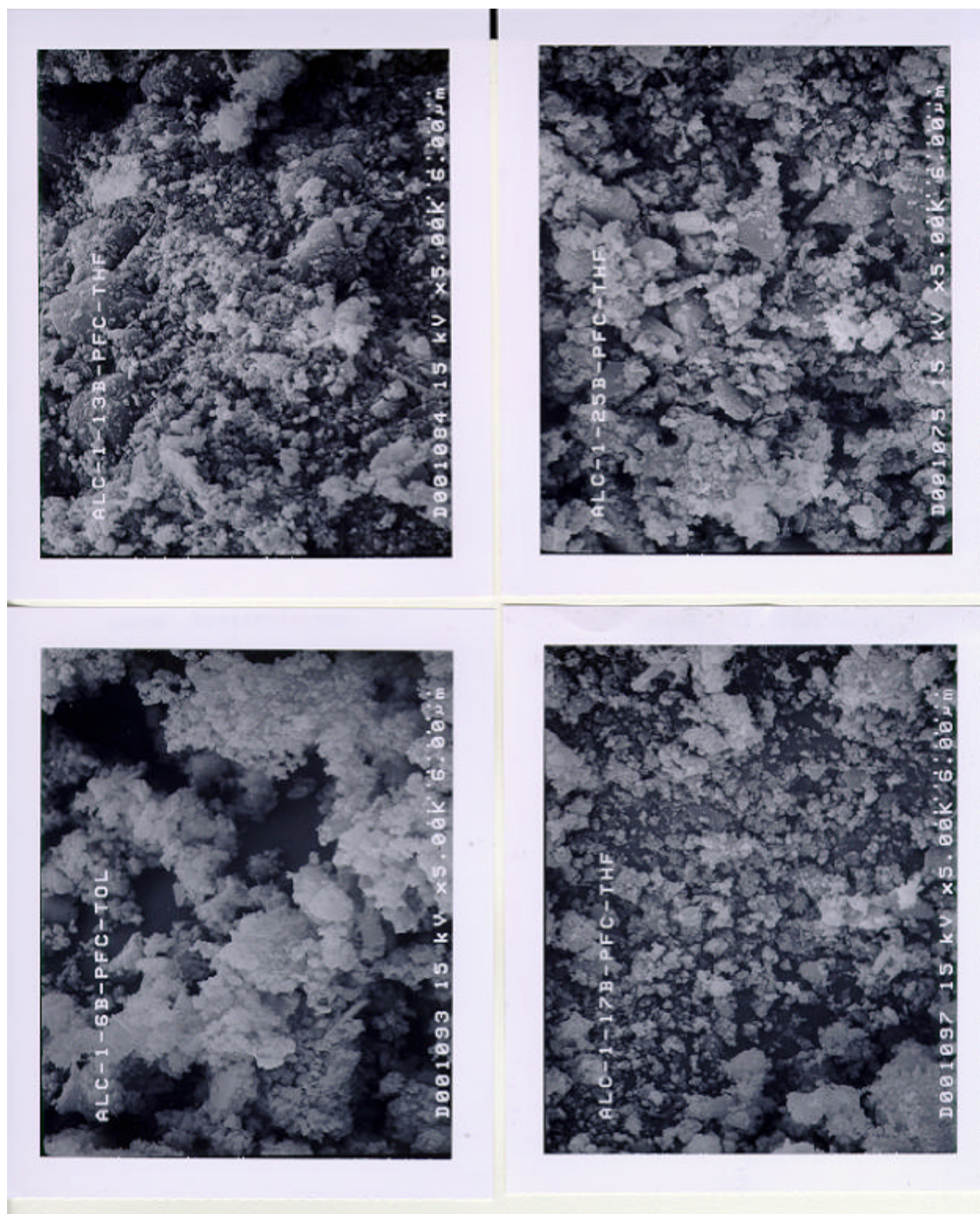


Figure 2
SEM Scans of ALC-2 Solids
Periods 7B, 18A and 21B

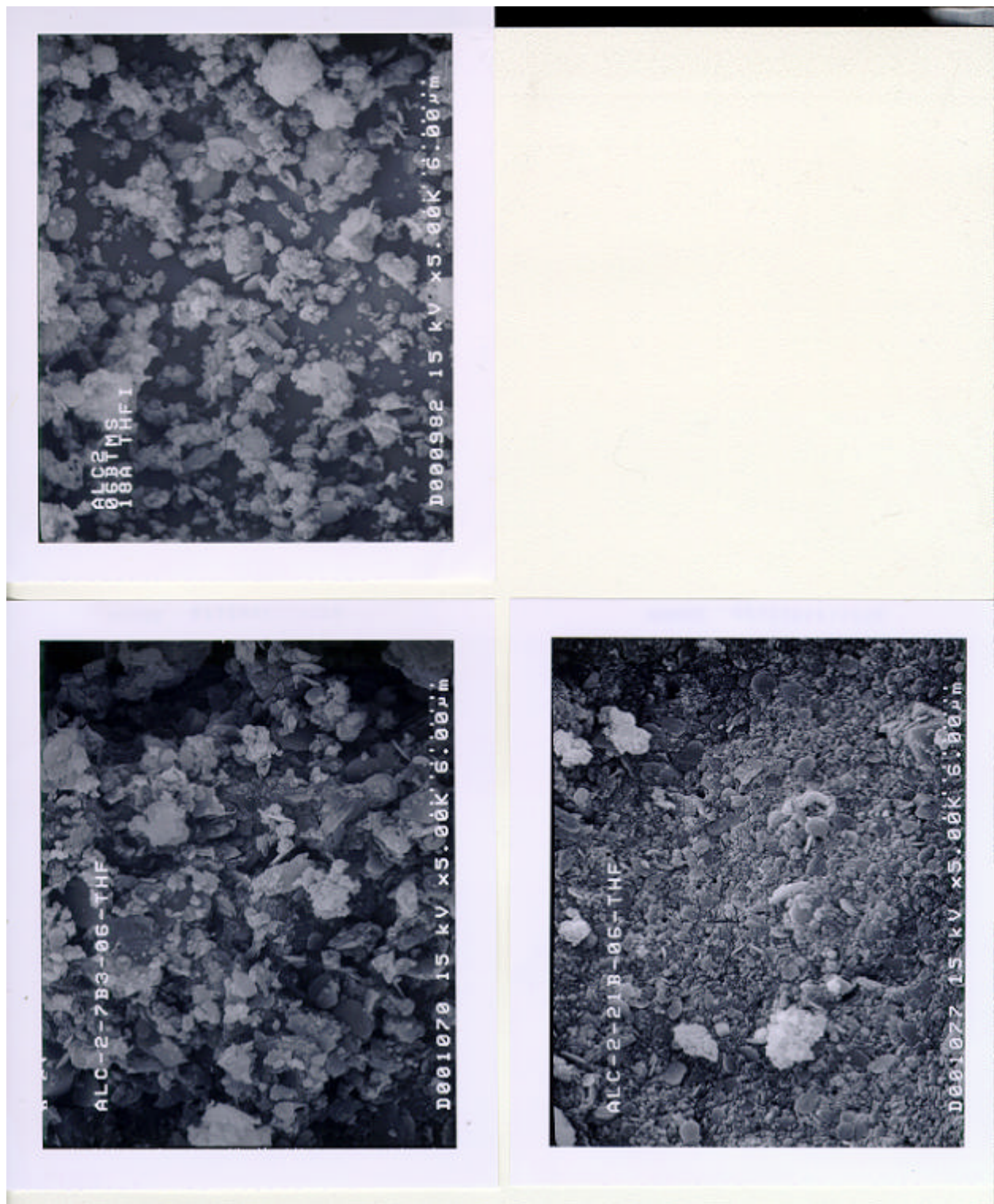


Figure 3
SEM Scans of Wilsonville Solids
Runs 258K and 262E

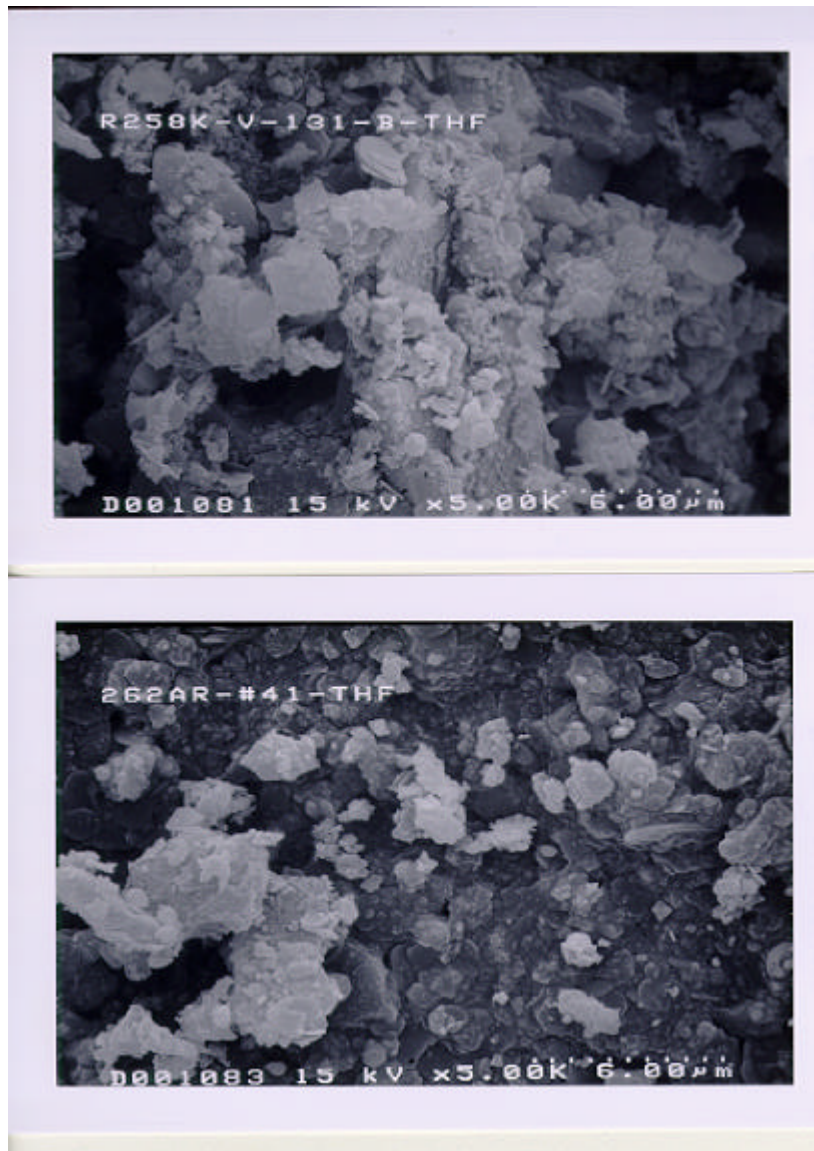
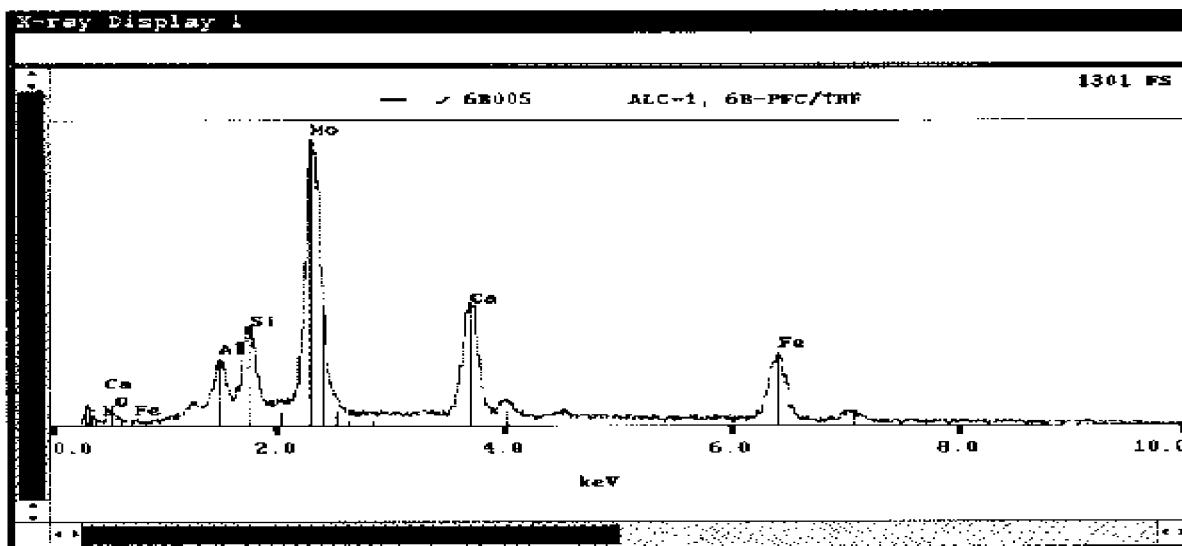


Figure 4
EDS Spectra of ALC-1 Solids

ALC-1-7B



ALC-1-13B

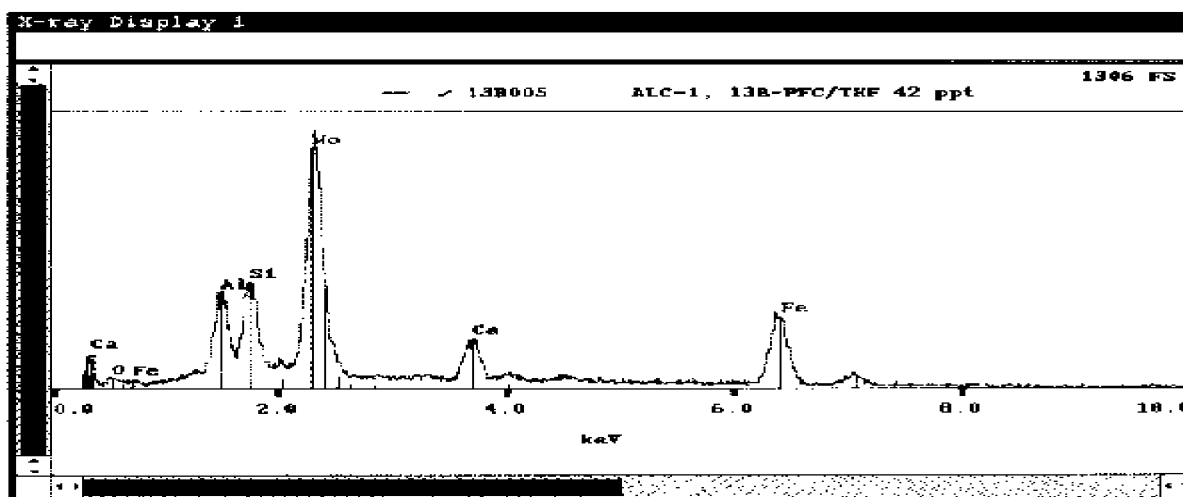
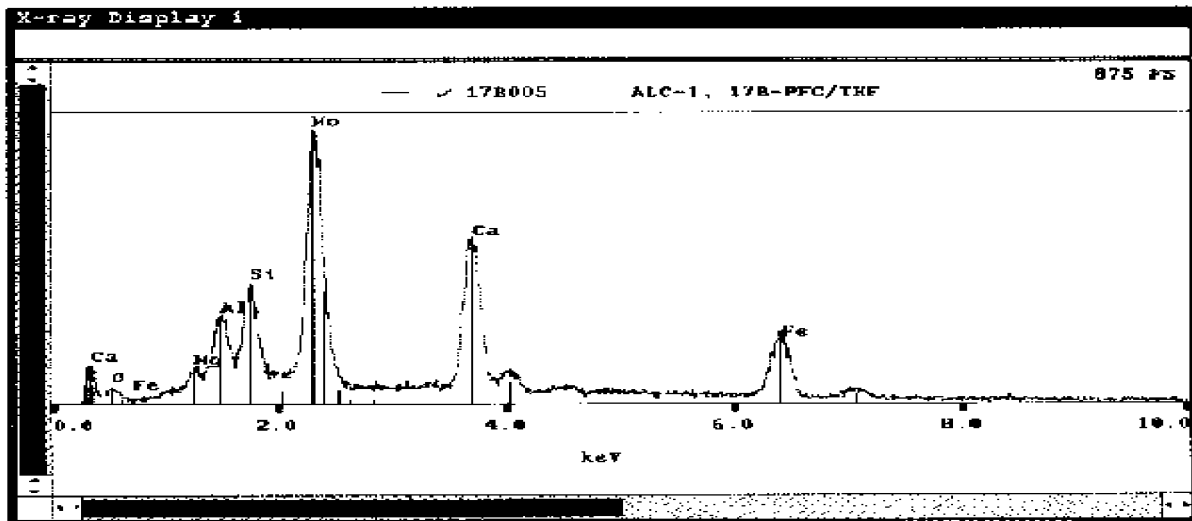


Figure 4 (Continued)

ALC-1-17B



ALC-1-20B

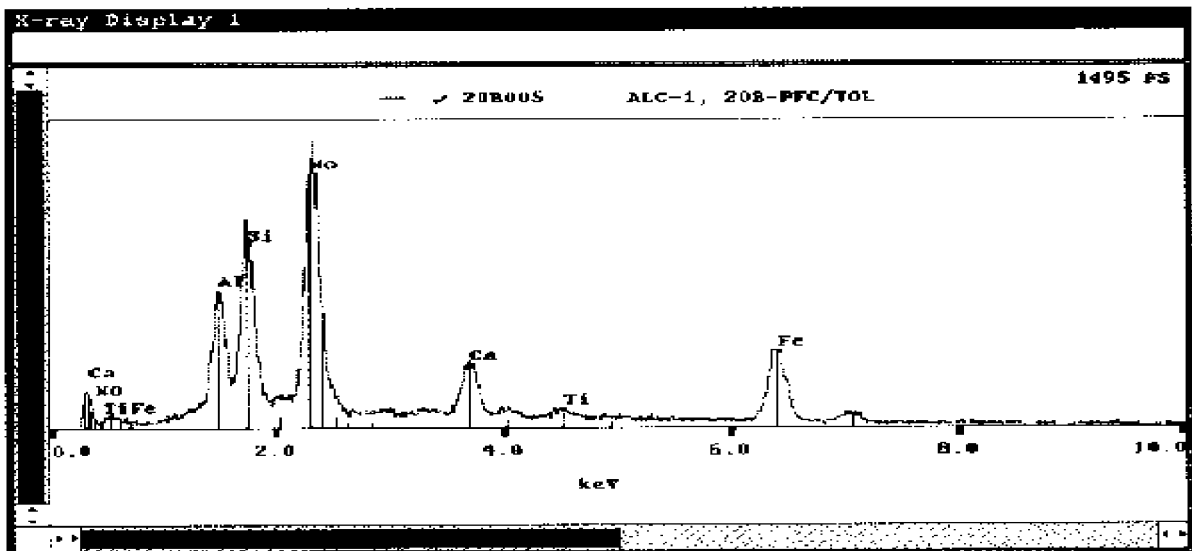


Figure 4 (Continued)

ALC-1-25B

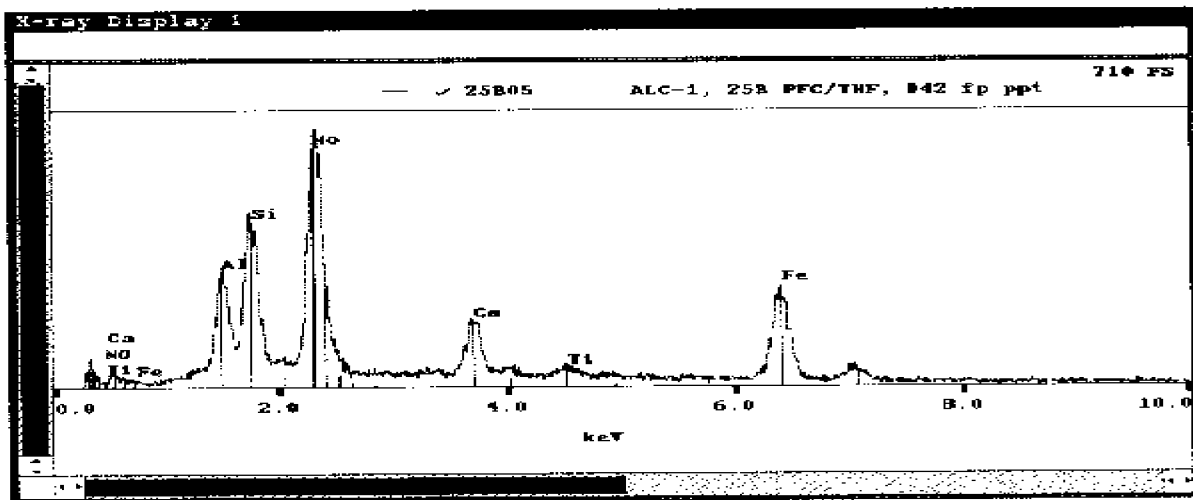
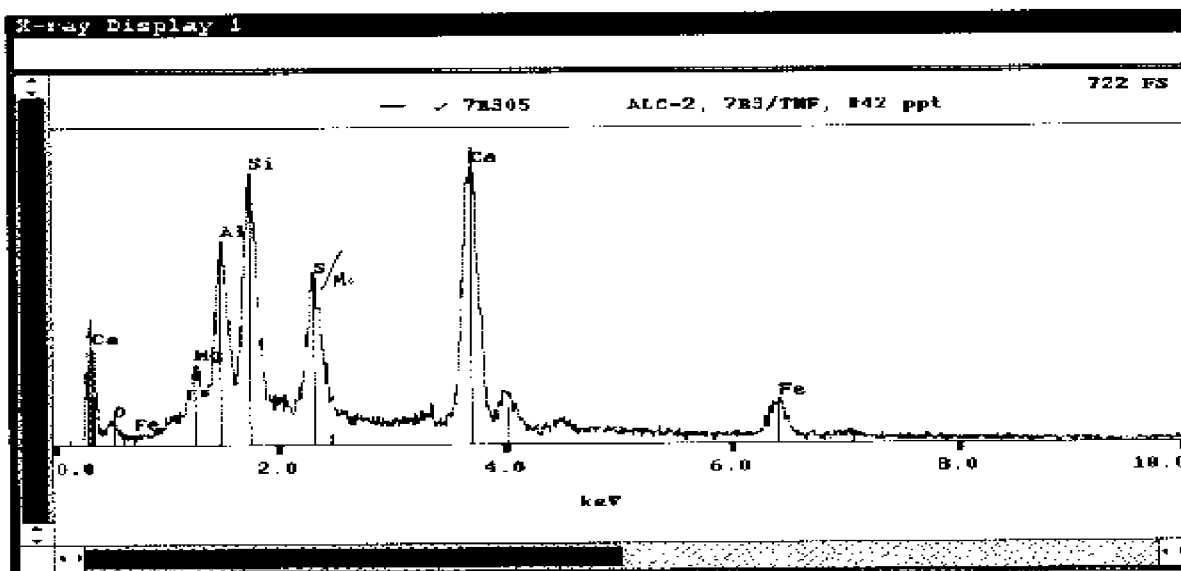


Figure 5
EDS Spectra of ALC-2 Solids

ALC-2-7B



ALC-2-18A

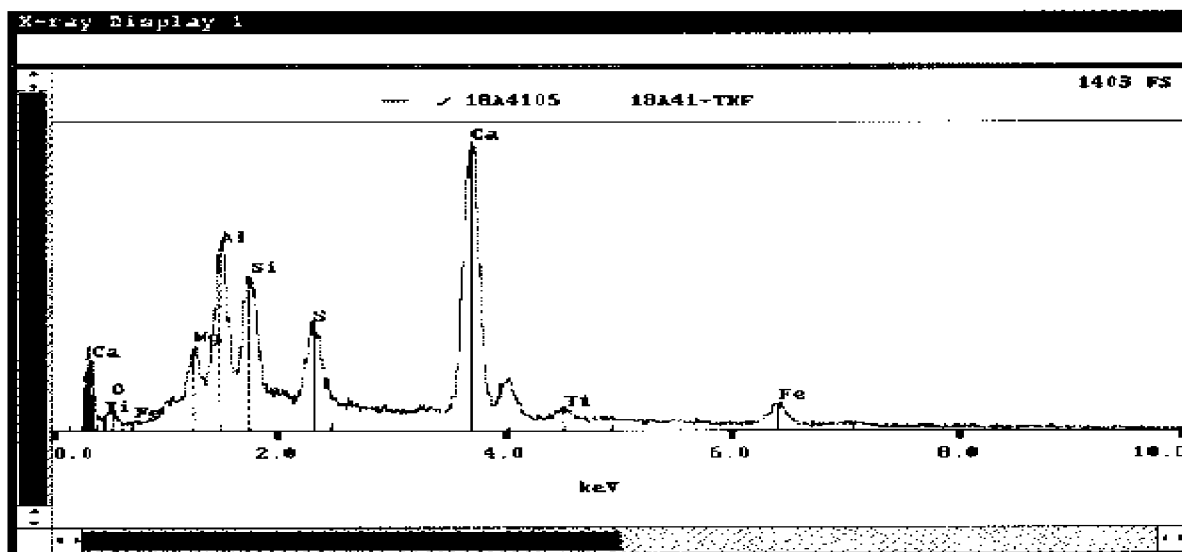


Figure 5 (Continued)

ALC-2-21B

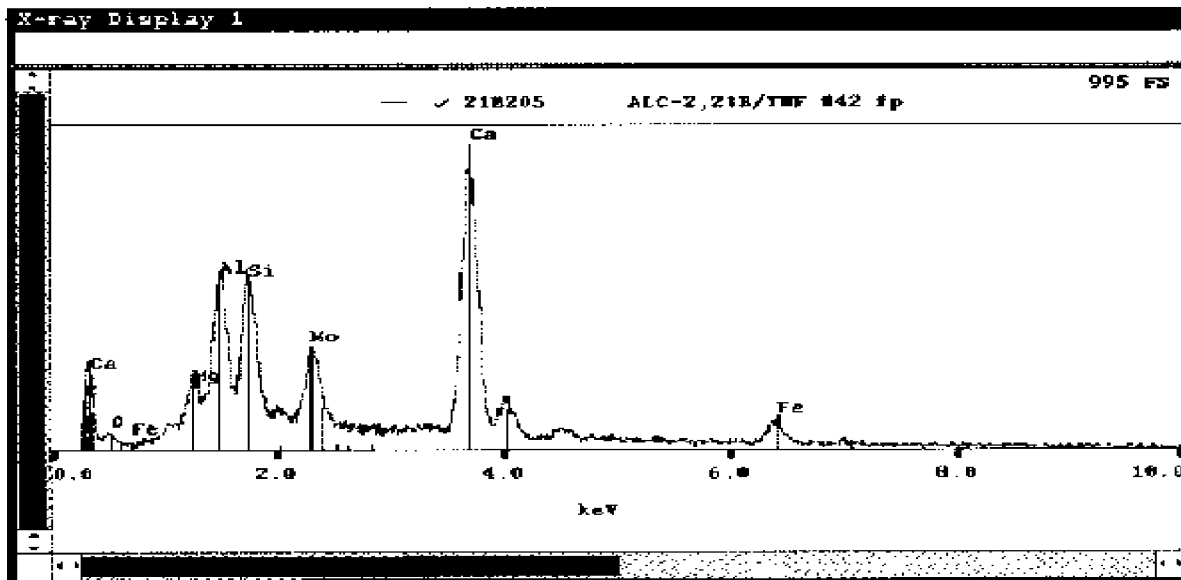
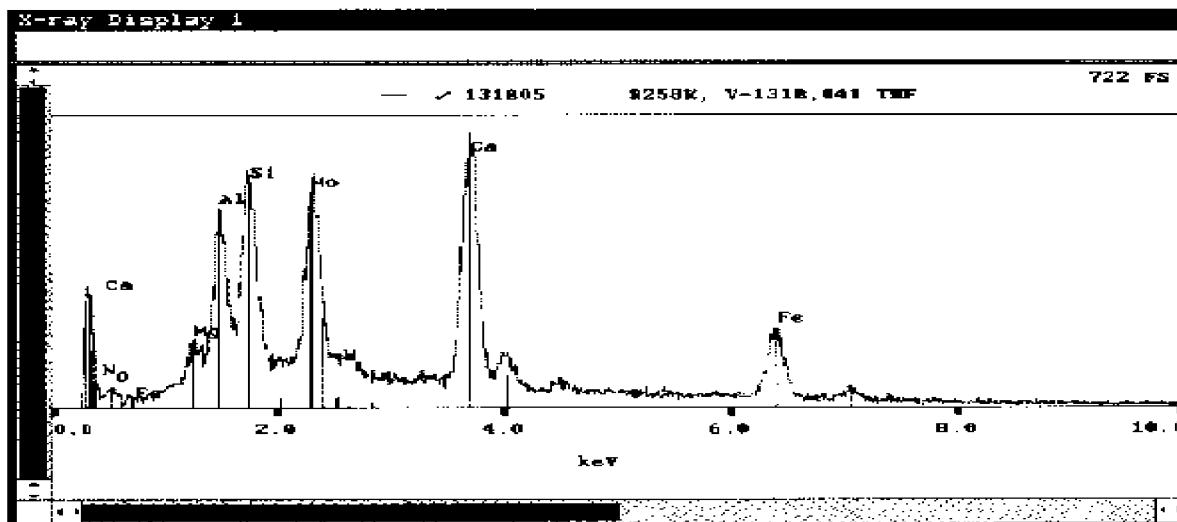


Figure 6
EDS Spectra of Wilsonville Solids

Run 258K



Run 262

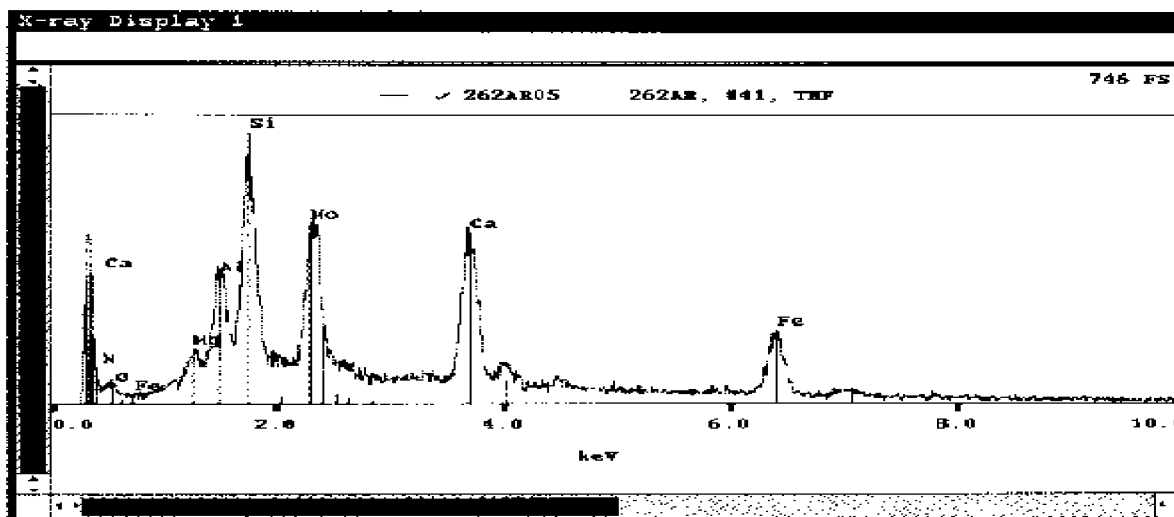


Figure 7
XRD Patterns of ALC-1 Solids

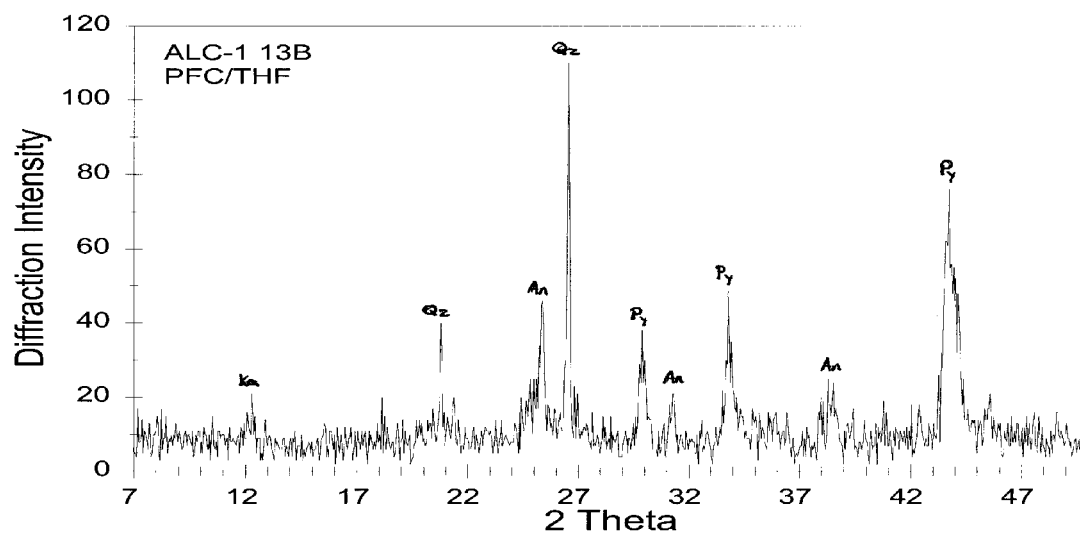
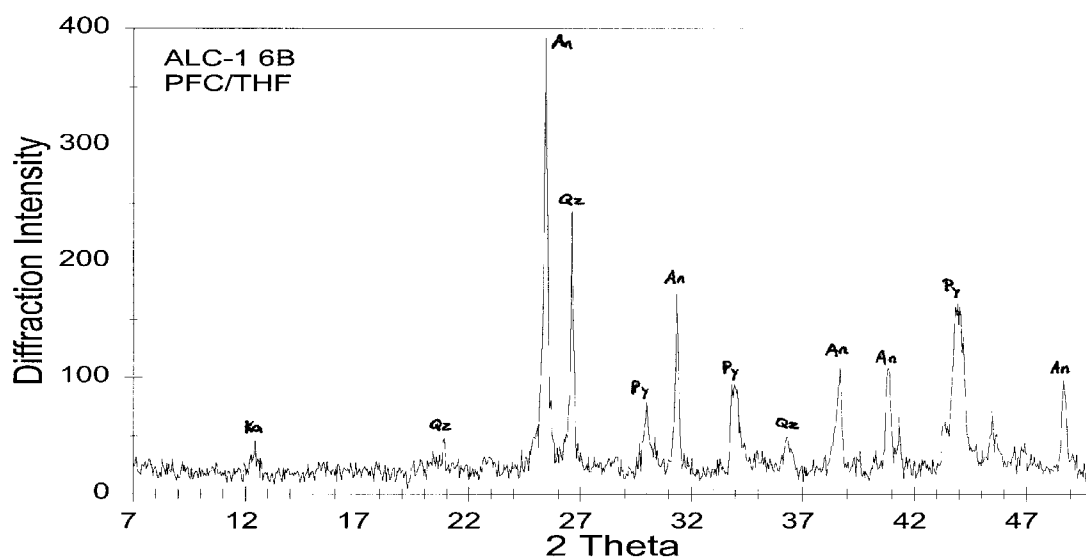


Figure 7 (Continued)
XRD Patterns of ALC-1 Solids

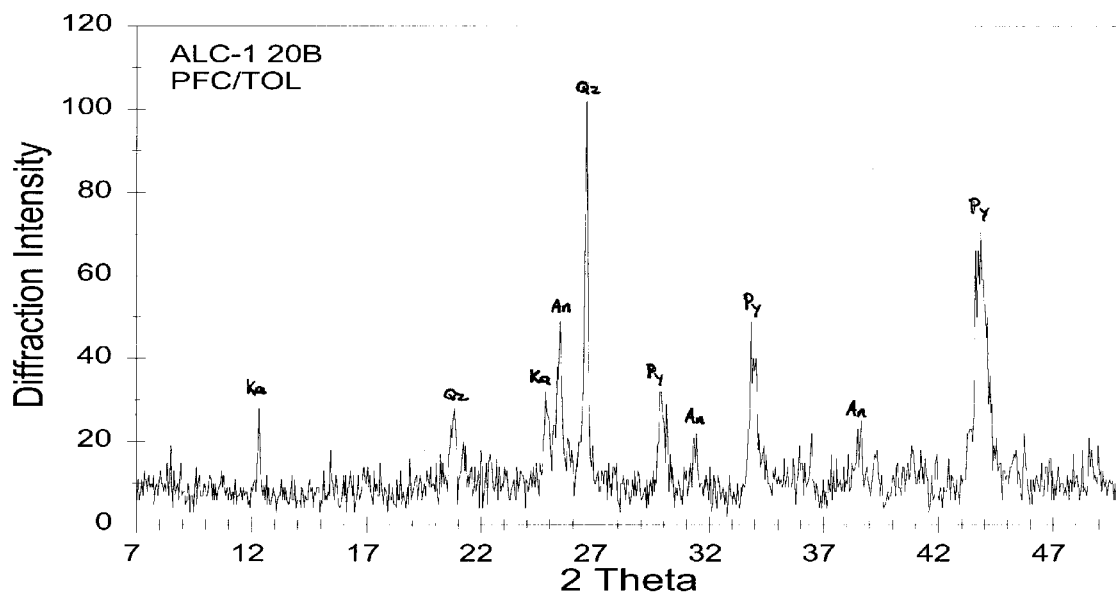
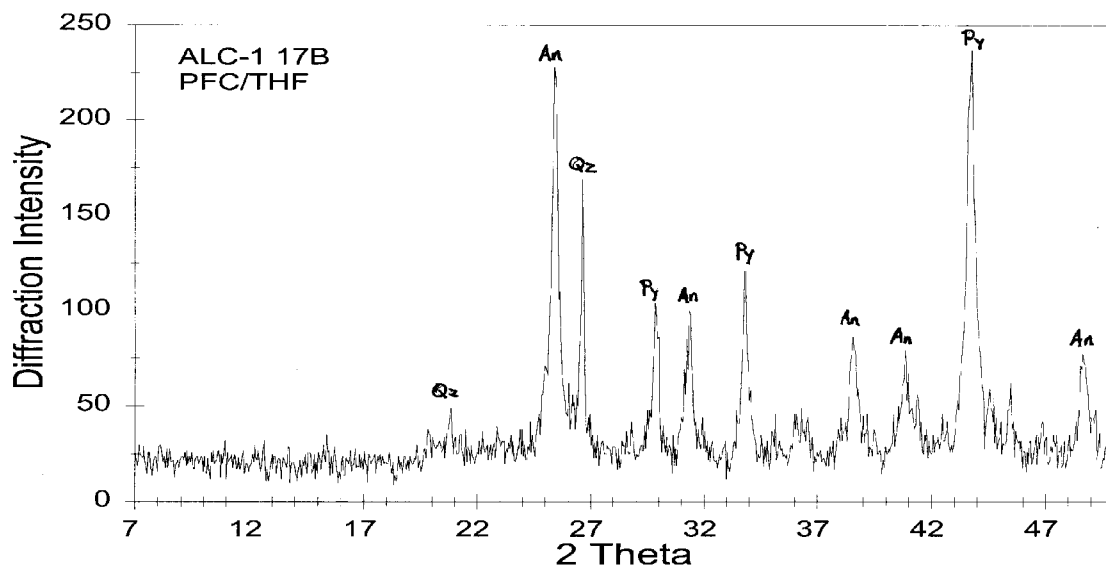


Figure 7 (Continued)
XRD Patterns of ALC-1 Solids

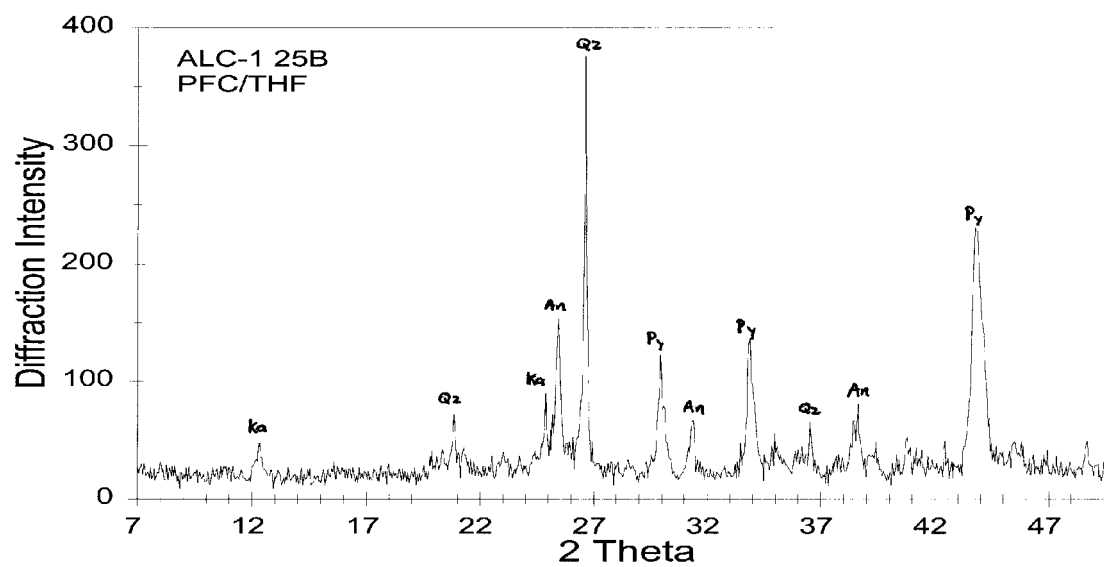


Figure 8
XRD Patterns of ALC-2 Solids

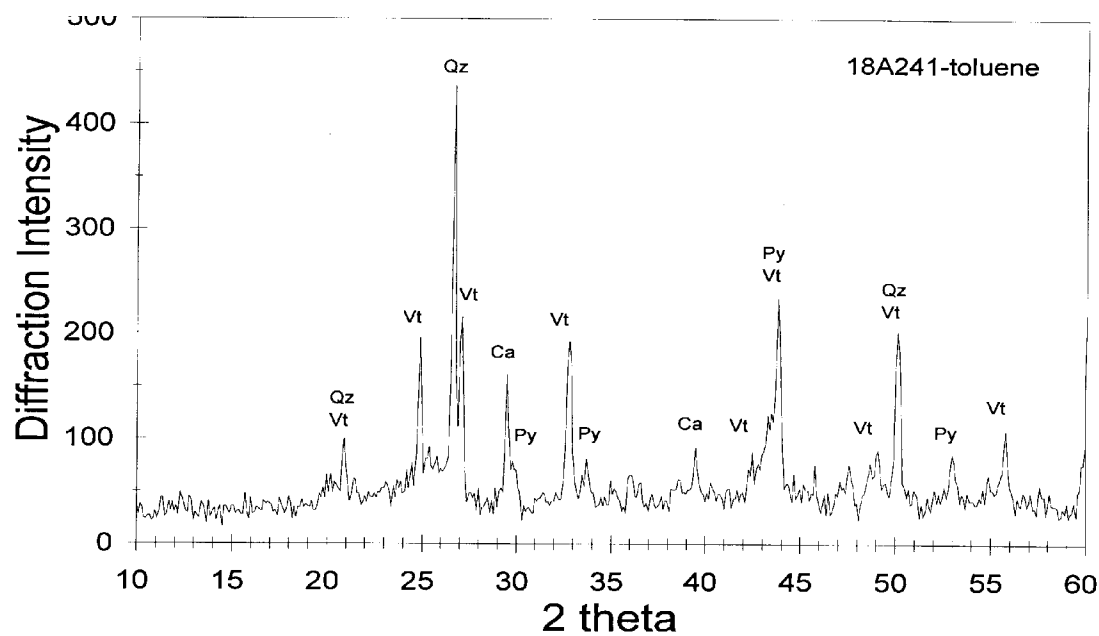
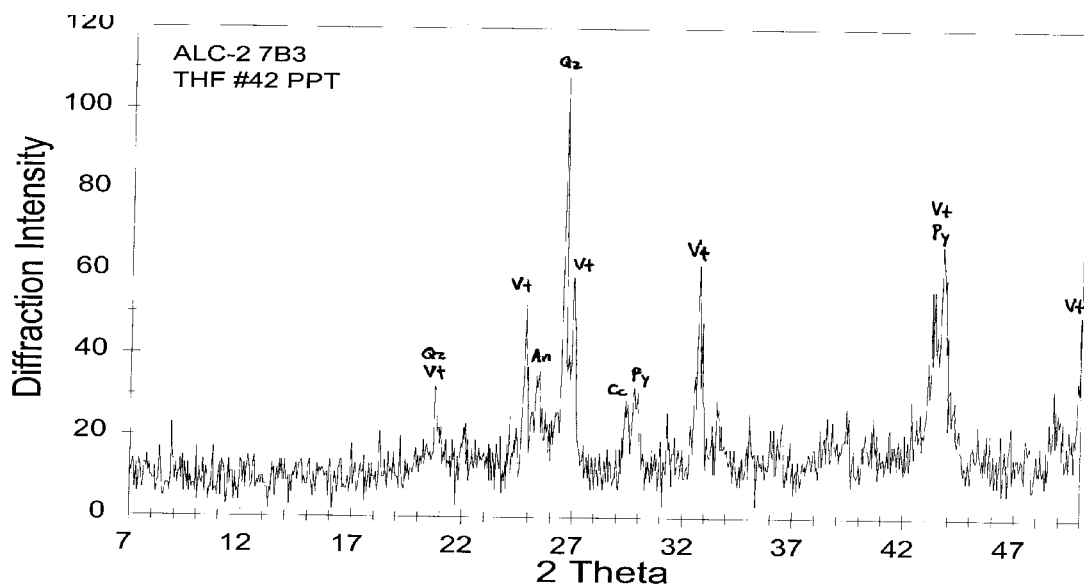


Figure 8 (Continued)
XRD Patterns of ALC-2 Solids

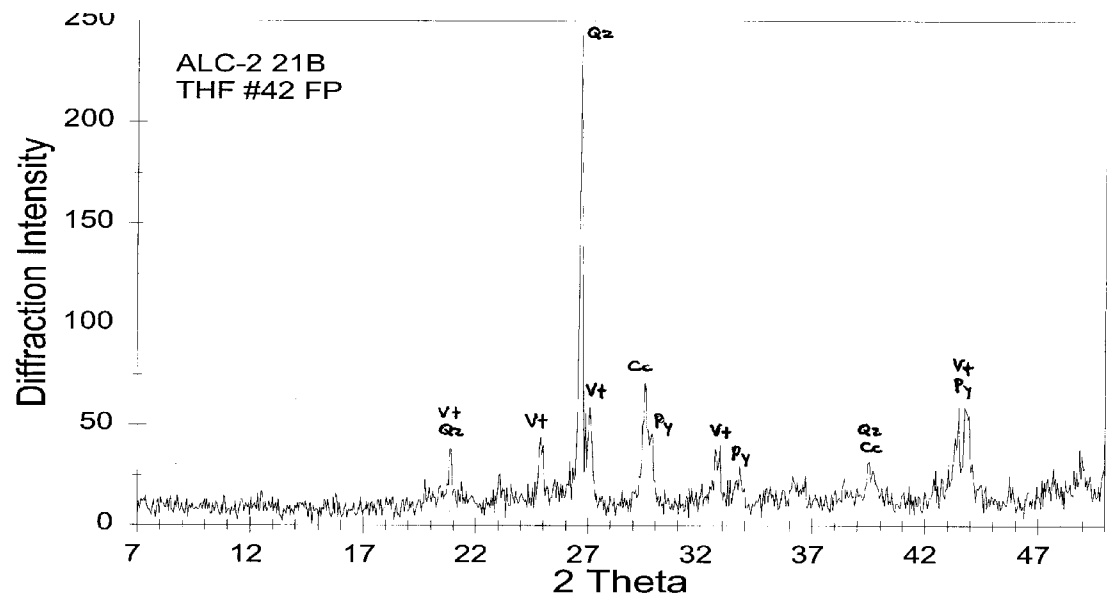


Figure 9
XRD Patterns of Wilsonville Solids

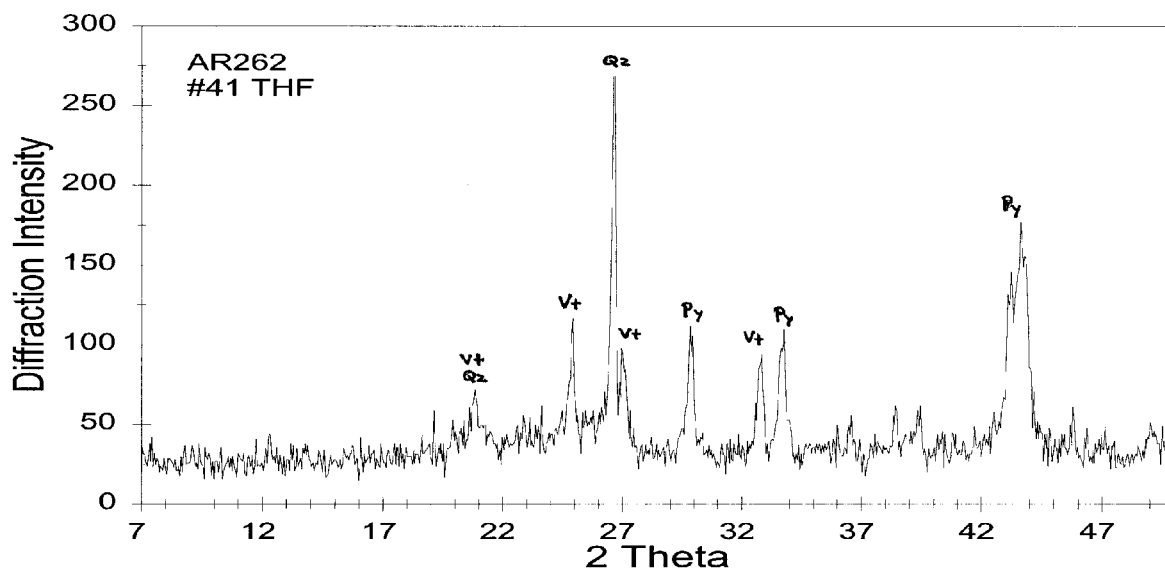
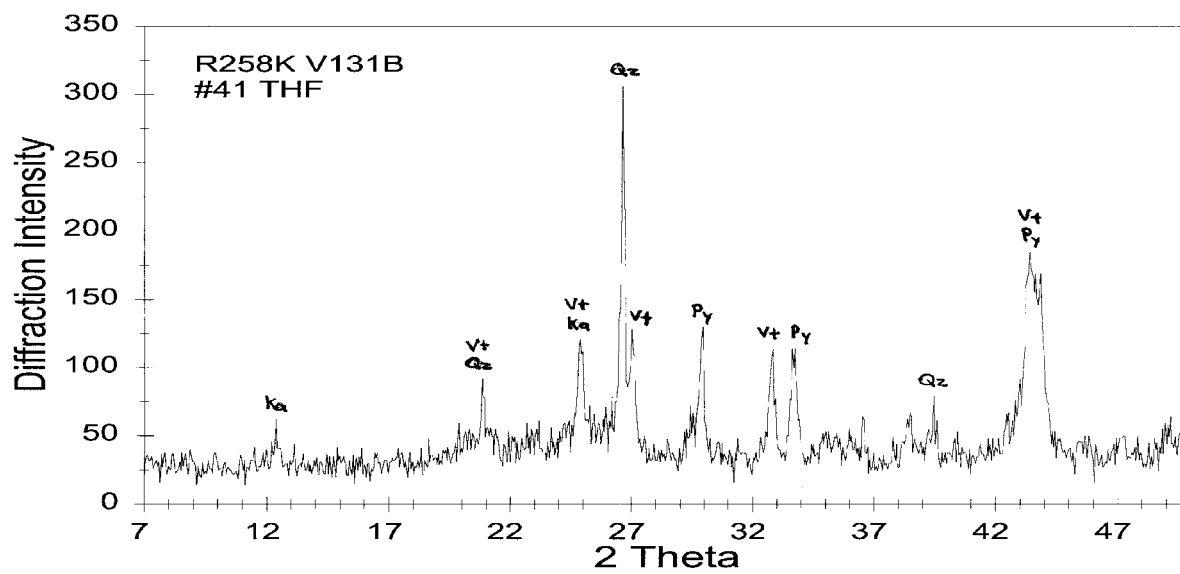


Figure 10. Feed Composition

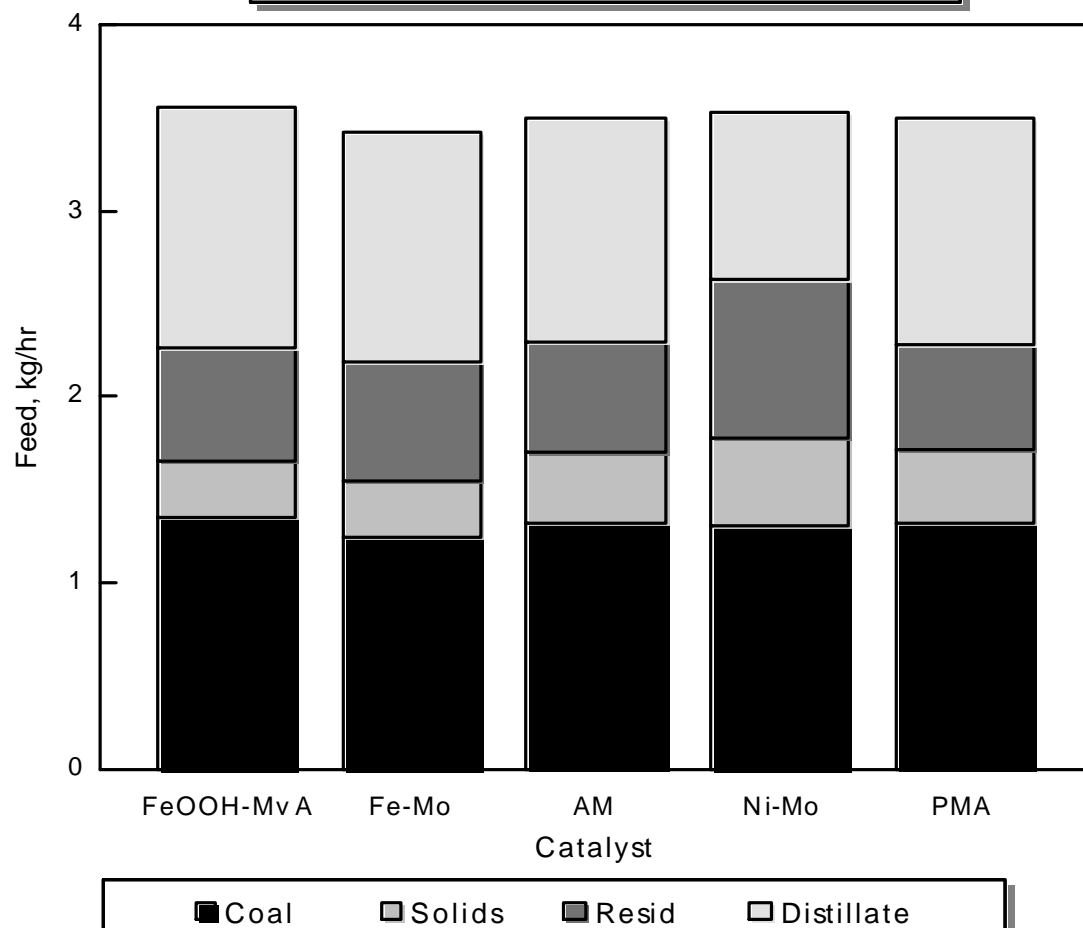
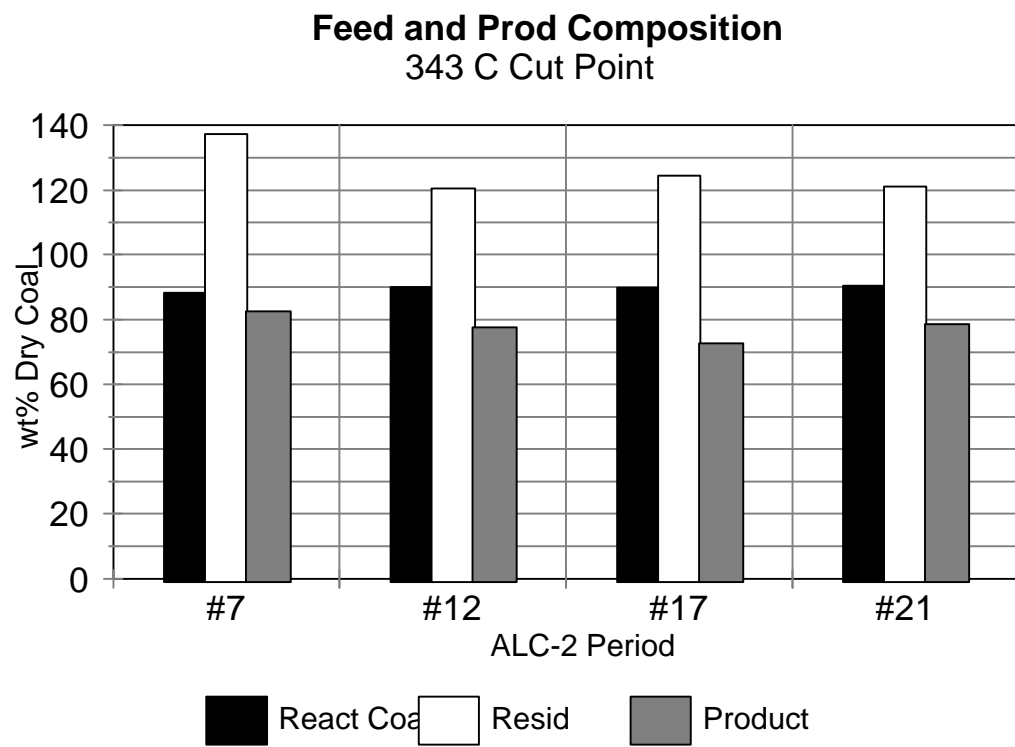


Figure 11



SECTION TWO

CONSOL, Inc.

(Report for Jan-Mar 1997)

September 17, 1997

Report Period: January 1 - March 31, 1997

SUBCONTRACT TITLE AND NUMBER:

Subcontract UKRF-4-25582-92-76 to CONSOL Inc.

Under DOE Contract No. DE-AC22-91PC91040, "Advanced Coal Liquefaction Concepts for the PETC Generic Bench-Scale Unit"

SUBCONTRACTOR NAME:

CONSOL Inc.

Research & Development

4000 Brownsville Road

Library, PA 15129

SUBCONTRACT PERIOD: November 26, 1991 - February 28, 1997 (future extension to September 30, 1998, expected)

PRINCIPAL INVESTIGATORS: R. A. Winschel, G. A. Robbins

SUBCONTRACT OBJECTIVES: No change.

SUMMARY OF TECHNICAL PROGRESS - OVERALL

Characterization work was completed on samples from HTI Run ALC-2 under DOE Contract DE-AC22-94PC93054. The major conclusions from CONSOL's analyses follow. Coal and oil properties provided no reason for the difficulties encountered in toluene extraction and pressure filtration. The concentrations of the catalytic metals Mo and Fe in the toluene-extracted solids samples from the first run condition were in the expected range, but the Ni concentration was higher than expected. Process oil properties generally were consistent for the entire run, suggesting that the distillation system was stable and that the choice of catalyst systems had little impact. The first-stage separator overhead (SOH) oils and the reduced-pressure still overhead (RPSOH) oils had very high phenolic -OH concentrations (containing perhaps 25% phenolics) and could be potential sources of chemical feedstocks. The properties of the hydrotreated product oils showed that all of the phenolics and most of the aromatic hydrogen were converted or removed. There are some systematic differences in the analyses reported by CONSOL and HTI for some elements; however, in general, the agreement on the coal analyses was quite good.

Future work includes: testing to evaluate methods for integrating catalyst addition with oil agglomeration in preparation for Run ALC-3. Agglomeration process modifications will be sought to improve performance and economics. Lab-scale slurry drying tests of agglomerates will be conducted in preparation for Run ALC-3.

SUMMARY OF TECHNICAL PROGRESS - BY TASK

Task 2 - Laboratory Support

Analysis of Samples from Run ALC-2

Thirty-two oil samples and four feed coal samples were received from HTI Run ALC-2 for characterization. Characterization of the samples was completed under DOE Contract DE-AC22-94PC93054.

Analysis of Feed Coals

Ten-pound samples were obtained of each of the four catalyst-treated Black Thunder coals used in Run ALC-2. The samples, which were shipped in 5-gallon pails, were stored in plastic bags after receipt. Analyses of the feed coals from Run ALC-2 were conducted with several goals in mind. Since ultra-fine particulate matter was suspected to have caused the poor performance in filtration and toluene extraction, the size distribution of the feed coal was determined. Another analysis goal was to evaluate the overall condition of the coals, since the coals were to be used as a feedstock during agglomeration testing in preparation for Run ALC-3. Complete coal analyses were obtained, and their suitability as agglomeration feeds was evaluated.

Coal size distribution was determined by wet screen analysis. To examine ultra-fine particulate, the -325 mesh fraction from wet screening was analyzed by the Malvern laser scattering instrument. The coal size distribution (Table 1) shows that the coals are not super-fine, and that they do not differ much in size consist. The wet screen analyses shows that the coals are 45-55% +200 mesh and 25-35% -325 mesh. There is a minor shift among the samples of about 10% of the material from the +200 mesh fraction to the -325 mesh fraction. These minor differences may reflect treatment time in the ribbon blender, since the coals treated with Ni or Fe in addition to Mo would have spent additional time in the blender. The d_{50} of the -325 mesh fractions were consistent at 28-30 μm . There is no indication of any unusual amount of ultra-fine material in these coals.

Other coal analyses (Table 1) included proximate and ultimate analyses, higher heating value, and major and trace ash elements. These results provide no indication of damage to the coals and, together with the size analyses, indicate that the coals are suitable agglomeration feedstocks. CONSOL's coal analyses were compared with those reported by HTI.¹ Relative to HTI analyses for the feed coals L-902, L-904, L-906, and L-911, (results uncorrected for ash- SO_3), CONSOL obtained results that were in generally good agreement on moisture (within

0.2 wt %), MF ash (within 0.1 wt %), MF carbon (within 0.7 wt %, CONSOL typically higher by ~0.6 wt %), MF hydrogen (CONSOL was consistently ~0.32 wt % lower), MF nitrogen (CONSOL was consistently ~0.05 wt % higher), MF sulfur (CONSOL was consistently 0.1-0.2 wt % higher); and MF oxygen by difference (CONSOL was typically ~0.5 wt % lower).

The HTI and CONSOL catalyst element concentrations in the ash are provided in Table 2. Relative to HTI analyses for the concentration of catalytic elements in the treated feed coals¹ (ash basis, uncorrected for ash-SO₃), CONSOL results were slightly lower for Mo (0.13-0.15 wt % for CONSOL vs. 0.15-0.18 wt % for HTI), higher for Fe (3.77-6.41 wt % for CONSOL vs. 3.18-5.25 wt % for HTI), and slightly lower for Ni (49-750 mg/kg for CONSOL vs. 49-829 mg/kg for HTI).

These results indicate that there are some systematic differences in concentrations reported by CONSOL and HTI. In general, however, the agreement between the CONSOL and HTI analyses was quite good. These results do not suggest a reason for the poor extraction and filtration of the product. They do indicate that the coals are suitable for developmental agglomeration tests in preparation of Run ALC-3.

Analysis of Condition 1 Toluene-Extracted Solids for Catalytic Metals

Selected CONSOL analyses of toluene-extracted solids (TES) are presented in Table 3. Relative to CONSOL analyses for the major elemental concentrations in the ash from of the treated feed coal L-902 (ash SO₃-free), CONSOL obtained results from TES sample ash (normalized SO₃- and K₂O-free) from Condition 1 that were: high for Na, high for Ca, high for Mg, slightly high for P, about the same for Al, quite low for Si, high for Ti, and not consistent for Fe. For the catalytic elements (Table 3), TES analyses varied significantly, but the averages are in the expected range for Mo and Fe. The concentration of Ni in the TES ash is much higher than in the feed coal ash. These results indicate that there is an unidentified source of Ni in the TES ash. Possible sources include contamination, vessel erosion, or analytical error. The analysis procedure is not expected to cause such an artifact, but further investigation is needed if the source of nickel contamination must be identified. Unfortunately, there are no HTI data on Ni concentrations in the continuous vacuum still bottoms (CVSB) samples from the early portion of the run (Table 2).

The concentrations of Fe measured by HTI in the CVSB sample ash (Table 2) were 28-58% higher than the concentrations in the feed coal ash for each corresponding operating condition.

The concentration of Ni measured by HTI in the CVSB ash was 24% lower than the corresponding concentration measured in the feed coal ash for Condition 3. Thus, the HTI data indicate that the Ni concentration may never have reached its target in the circulating oil.

Analysis of Oils From Run ALC-2

The THF-soluble portions of several continuous vacuum still bottoms (CVSB) samples were separated into oil, asphaltene, and preasphaltene fractions by preparatory liquid column separation (LCF). The intent was to identify the causes of the poor extraction and filtration performance of this stream in segments of Run ALC-2. The solubility component distributions and other data were very similar for samples taken before, during, and after the troublesome portion of the run. Attempts to characterize individual preasphaltene fractions by FTIR or ¹H-NMR were unsuccessful. Thus, nothing was found to relate to poor extraction and filtration performance of the CVSB stream.

Coal-Oil Agglomeration Work In Preparation For Run ALC-3

Laboratory agglomeration work was begun in preparation of Run ALC-3. Several unsuccessful attempts were made to emulsify No. 6 fuel oil with water and a non-ionic surfactant. Once an emulsion is made, it will be tried as an agglomerating oil with Black Thunder Mine coal. These experiments are designed to reduce the thermal requirements for oil-agglomeration.

Information was obtained from the literature that provides useful information on oil agglomeration economics. The information was provided to LDP Assoc.

Characterization of Sandia Hydrotreating Product Samples

One feed oil and seven product oils were received from hydrotreating tests at Sandia National Laboratory. These materials were characterized by elemental analysis, NMR for proton distribution, and FTIR for phenolic -OH concentration. Most were tested in the microautoclave for solvent quality. The feed oil was a 524 °C⁻ (975 °F⁻) vacuum still overhead (VSOH) distillate from the pressure-filter liquid (PFL) oil from period 16B, Condition 4, of HTI Run PB-01 (227-90). Although 100% Hondo oil was fed in Condition 4, the sample was taken within a day after completing 5 days of operation with Black Thunder Mine coal in Condition 3. A description of the hydrotreating runs and Sandia's data on the feed and product materials is provided elsewhere.² Sandia performed these runs to determine if less-severe hydrotreating conditions would provide good hydrogenation, but with less cracking (production of low-boiling components) than was observed in previous hydrotreating tests. Sandia's earlier tests and

CONSOL's analyses of samples from those tests were reported earlier.³ Sandia will use the data provided to finalize their conclusions and recommendations. However, they found that significant reductions in product boiling-point distributions occurred at unexpectedly mild hydrotreating conditions.²

Sandia found that the boiling point distributions of the hydrotreated oils were affected by hydrotreating conditions. Hydrotreating decreased the product boiling point, relative to the feed (refer to the hydrotreating conditions reproduced in Table 4; Reference 2 contains complete details). Increasing the reaction temperature over the 345-385 °C range decreased the product boiling point distribution:

feed > sample 107-830-96A > sample 107-829-96A > sample 107-828-96A.

Decreasing the weight hourly space velocity (WHSV) over the 1-3 g feed/g cat-hr range decreased the product boiling point distribution:

feed > sample 107-911-96B > sample 107-829-96A > sample 107-905-96B.

Increasing the hydrogen pressure over the 500-1800 psig range decreased the product boiling point distribution:

feed > sample 107-913-96B > sample 107-906-96C > sample 107-829-96A.

CONSOL's analytical results for these samples are presented in Tables 4 and 5. Some of the product samples had a strong ammonia odor that may indicate those samples were not entirely stripped of dissolved gases. Thus, some fraction of the nitrogen (and possibly sulfur) content of the products may not be a component of the liquid product. The samples are listed in the tables in order of decreasing nitrogen and sulfur content, a reflection of increased hydrotreating effectiveness. The hydrotreating conditions provided by Sandia, and CONSOL's elemental analyses, phenolic -OH concentrations and peak positions obtained by FTIR, and summarized proton (hydrogen) distributions obtained by NMR are shown in Table 4. The full set of the CONSOL NMR proton distribution results are shown in Table 5. There is some scatter in the carbon determinations (Table 4). Two of the hydrogen determinations are suspect (particularly for sample 107-830-96A), and the oxygen contents by difference are highly variable and do not appear to be trustworthy. Virtually all of the results for nitrogen, sulfur, phenolic -OH

concentration and peak position, and proton distribution consistently show the same trend of decreasing heteroatom and increasing hydrogen concentration with presentation order in the table. Generally, the ranking of conditions (temperature, hydrogen pressure, and space velocity), based on CONSOL's analytical data and Sandia's product boiling-point data agree well, with a low boiling point indicating effective hydrotreating. Thus, the boiling point distributions of the product oils (Sandia's data) generally decrease in the same order as moving down Table 4.

The last two samples in the tables, samples 107-828-96A and 107-905-96B, are essentially equivalent in heteroatom content, but seem to differ slightly in hydrogen content and hydroaromatic hydrogen content. Both of these values are slightly higher for 107-828-96A than for 107-905-96B. The results indicate more hydrogenation at 385 °C and WHSV = 2 than at 365 °C and WHSV = 1, but essentially equivalent heteroatom removal at both conditions.

Although the microautoclave data appear to have more scatter than expected, there is a strong indication that the products, except the one produced at the mildest conditions, have improved solvent qualities. For example, most of the products gave coal conversions of about 83%, whereas the feed gave coal conversions of 72% and 76% in repeat tests.

Distribution of Samples

As requested by E. N. Givens, 100 g of O-6 bottoms from period 7 of Run ALC-2 and samples of toluene-extracted pressure-filter cakes from Run ALC-1 were sent to CAER. At the request of J. Hu, aliquots of two interstage slurry samples from Run ALC-2 were sent to HTI.

Task 3 - Continuous Operations

We reviewed and discussed with HTI and LDP Associates their preliminary material balance calculation for Run ALC-2.

Discussions were held with HTI personnel concerning the possibility of performing oil agglomeration and slurry drying of the agglomerated coal at HTI during Run ALC-3. Slurry drying has been successfully performed at HTI with coals containing up to about 27% moisture (about 35% moisture is expected in the fresh agglomerates). Slurry drying tests performed at CONSOL would be used to establish drying conditions. A test in the slurry mix tank at HTI would be required prior to a liquefaction run. Although HTI indicates that they could easily construct an agglomeration vessel, they would need to obtain a suitable stirring motor. Options

under consideration are the loan of CONSOL's equipment (if relatively large batches are prepared), or construction of a smaller vessel for more frequent small batches. One batch of the same quantity of agglomerates produced for Run ALC-1 would provide approximately one day of feed to the liquefaction unit. Small batches made more frequently would reduce the oil inventory requirement, allow easier handling (perhaps enabling one person to make each agglomeration run), and increase the frequency of the runs, which would better integrate agglomeration with the liquefaction process.

Task 4 - Technical Assessment

The quarterly Technical Progress Report for April through June was revised per DOE comments and issued. The reports for July through September and October through December 1996 were issued. An electronic copy of the October-December 1996 report was provided to CAER to comply with DOE's new electronic reporting format.

The International Conference on Coal Science accepted CONSOL's abstract "Oil Agglomeration at Low pH as a Pretreatment for Liquefaction of Wyoming (USA) Subbituminous Coal".

Results of CONSOL's characterization of samples from HTI Run ALC-2 were presented at the post-run meeting at HTI.

CONSOL's comments were provided on HTI's draft report on Run ALC-2; they will issue an expanded version of the report for a second review.

R. A. Winschel
Project Manager

/ls

References

1. Hu, J. "Advanced Direct Liquefaction Concepts Program, Phase II, Run ALC-2 Draft Report", U. S. DOE, Contract No. DE-AC22-91PC91040, March 1997.
2. Miller, J. E. Draft quarterly report to DOE-PETC, cover letter to G. A. Robbins dated October 30, 1996.
3. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Advanced Coal Liquefaction Concepts For the PETC Generic Bench-Scale Unit, Quarterly Technical Progress Report for April through June 1996", Subcontract UKRF-4-25582-92-76 under DOE Contract DE-AC22-91PC91040, September 18, 1996.

TABLE 1

CHARACTERISTICS OF CATALYST-TREATED COALS FED IN HTI RUN ALC-2

	Coal Sample and Run ALC-2 Condition Number			
	L-902 Cond. 1	L-904 Cond. 2	L-906 Cond. 3	L-911 Cond. 4
Moisture, wt % As-Determined	12.68	13.07	10.46	11.16
Ash, wt % MF, Including SO ₃	6.78	6.07	6.26	6.13
SO ₃ Content Used to Correct Ash	18.95	17.11	16.73	16.86
Ash, wt % MF, SO ₃ -Free	5.50	5.03	5.21	5.10
<u>Proximate, wt % MF, SO₃-Free Ash Basis</u>				
Volatile Matter	46.58	46.58	46.68	47.07
Fixed Carbon	47.92	48.39	48.11	47.83
Heating Value, Btu/lb MAF, SO ₃ -Free Ash Basis	12627	12647	12697	12663
<u>Ultimate, wt % MF, SO₃-Free Ash Basis</u>				
C	70.33	70.71	70.81	70.05
H	4.75	4.82	4.78	4.80
N	1.07	1.03	1.04	1.04
S, Total	0.58	0.46	0.48	0.48
O (by Difference)	17.77	17.95	17.68	18.53
<u>Major Ash Elements, Oxide wt % of SO₃-Free Ash</u>				
MoO ₃	0.28	0.29	0.23	0.23
NiO	0.01	0.01	0.11	0.01
Na ₂ O	1.57	1.69	1.65	1.68
K ₂ O	0.47	0.54	0.54	0.49
CaO	26.67	27.58	26.68	26.83
MgO	5.43	5.60	5.58	5.65
Fe ₂ O ₃	11.30	6.83	6.70	6.48
TiO ₂	1.44	1.42	1.50	1.50
P ₂ O ₅	1.22	1.29	1.22	1.25
SiO ₂	34.62	35.84	36.17	35.37
Al ₂ O ₃	18.10	18.13	19.01	18.50
Total	101.11	99.23	99.41	98.02
<u>Sieve Size, Fraction wt % of Total</u>				
+48 mesh	0.0	0.0	0.3	0.4
48 x 100 mesh	7.8	4.2	7.8	6.0
100 x 200 mesh	36.5	42.2	39.4	47.5
200 x 325 mesh	19.2	25.1	20.4	20.8
-325 mesh	36.5	28.5	32.1	25.3
<u>Particle Size Analysis of -325 mesh Fraction (a), μm, vol % distribution</u>				
d ₁₀	8.08	8.14	7.88	8.97
d ₅₀	28.53	27.67	28.87	30.58
d ₉₀	55.85	50.12	55.43	54.47
Mo wt % of SO ₃ -free ash	0.19	0.19	0.16	0.16
Fe wt % of SO ₃ -free ash	7.90	4.78	4.69	4.53
Ni mg/kg of SO ₃ -free ash	60	75	901	59
Mo wt % of SO ₃ -containing ash	0.15	0.16	0.13	0.13
Fe wt % of SO ₃ -containing ash	6.41	3.96	3.90	3.77
Ni mg/kg of SO ₃ -containing ash	49	62	750	49

(a) by Malvern laser scattering

TABLE 2
CONCENTRATIONS OF CATALYTIC METALS IN ASHY STREAMS
FROM HTI RUN ALC-2

Sample	Cond. No.	Analyzed by	Basis	Metal Concentration in Ash		
				Mo, wt %	Fe, wt %	Ni, mg/kg
Per. 1-7 CVSB(a)	1	HTI ¹	Ash SO ₃ Uncorrected	0.17	6.70	NA
Per. 8-12 CVSB	2	HTI ¹	Ash SO ₃ Uncorrected	0.15-0.19	5.01-6.65	NA
Per. 13-17 CVSB	3	HTI ¹	Ash SO ₃ Uncorrected	0.17-0.20	4.63-5.01	184-631
Per. 18-21 CVSB	4	HTI ¹	Ash SO ₃ Uncorrected	0.16	4.59-4.75	404-565
Coal L-902	1	HTI ¹	Ash SO ₃ Uncorrected	0.16	5.25	49
Coal L-904	2	HTI ¹	Ash SO ₃ Uncorrected	0.18	NA	NA
Coal L-906	3	HTI ¹	Ash SO ₃ Uncorrected	0.15	3.18	829
Coal L-911	4	HTI ¹	Ash SO ₃ Uncorrected	0.15	3.41	67
Coal L-902	1	CONSOL	Ash SO ₃ Uncorrected	0.15	6.41	49
Coal L-904	2	CONSOL	Ash SO ₃ Uncorrected	0.16	3.96	62
Coal L-906	3	CONSOL	Ash SO ₃ Uncorrected	0.13	3.90	750
Coal L-911	4	CONSOL	Ash SO ₃ Uncorrected	0.13	3.77	49
Coal L-902	1	CONSOL	Ash SO ₃ -Free	0.19	7.90	60
TES Samples, Compare with Coal L-902						
Per. 2AB TES	1	CONSOL	Norm. SO ₃ - and K ₂ O- Free	0.15	7.41	258
Per. 3B TES	1	CONSOL	Norm. SO ₃ - and K ₂ O- Free	0.22	10.04	331
Per. 5AB TES	1	CONSOL	Norm. SO ₃ - and K ₂ O- Free	0.07	4.63	125
Per. 6 TES	1	CONSOL	Norm. SO ₃ - and K ₂ O- Free	0.21	8.69	135

(a) HTI analyzed only the period 7 sample.

NA = not available

TABLE 3

**CHARACTERISTICS OF TOLUENE-EXTRACTED SOLIDS FROM CONDITION 1
OF HTI RUN ALC-2**

	TES Sample and Run ALC-2 Period Number			
	Per. 2AB	Per. 3B	Per. 5AB	Per. 6
Toluene, wt % As-Determined (By Evaporation)	10.4	2.8	15.0	25.7
Ash, wt % As-Determined, Including SO ₃ (a)	7.95	25.03	10.04	10.45
Unaccounted, wt % of SO ₃ -Containing Ash (b)	21.94	16.80	20.34	21.80
Ash, wt % As-Determined, Calculated, SO ₃ - and K ₂ O-Free (c)	6.21	20.82	8.00	8.17
<u>Major and Minor Ash Elements, Oxide wt % of SO₃- and K₂O-Free Ash (c)</u>				
MoO ₃	0.22	0.34	0.10	0.32
NiO	0.03	0.04	0.02	0.02
Na ₂ O	2.39	2.14	2.19	2.14
CaO	33.59	30.44	33.59	36.64
MgO	7.21	6.29	7.05	7.71
Fe ₂ O ₃	10.60	14.35	6.61	12.42
TiO ₂	2.15	1.84	2.09	2.25
P ₂ O ₅	1.48	1.43	1.43	1.68
SiO ₂	23.44	25.17	27.55	18.32
Al ₂ O ₃	18.88	17.97	19.37	18.50
<u>Metal Concentration in SO₃- and K₂O-Free Ash</u>				
Mo, wt %	0.15	0.22	0.07	0.21
Fe, wt %	7.41	10.04	4.63	8.69
Ni, mg/kg	258	331	125	135

- (a) ASTM ash of whole sample.
- (b) Weight percent of ASTM ash that was not accounted for by summing the contributions of oxides determined (SO₃ and K₂O not determined).
- (c) Element concentrations were determined on an as-determined basis by digestion of the whole sample and analysis via a procedure that did not include sulfur and potassium (the digestion procedure adds potassium). Normalized SO₃- and K₂O-free ash content was obtained by summing all of the elemental concentrations in their oxide forms.

TABLE 4

**SAMPLE GENERATION CONDITIONS AND CONSOL ANALYSES OF SAMPLES
FROM SANDIA HYDROTREATING TESTS**

Sample	Temp, °C	H ₂ Pres, psig(a)	WHSV, g feed/g cat-hr	C, %	H, %	N, %	S, %	O(Diff), %	Phen. OH Conc., meq/g	MAC Conv. (f)	Proton Distribution, %		
											Arom . (b)	H-Arom. (c)	Par. (d)
PFL-VSOH 227-90-16B (Feed)				88.46	9.36	0.76	0.98	0.44	0.77	76.3/71.9	24.3	11.5	40.7
07-913-96B	365	500	2	89.01	9.34	0.69	0.43	0.53	0.52	74.4	23.4	12.3	41.2
07-830-96A	345	1800	2	88.94	8.99 ^e	0.56	0.37	1.14	0.44	83.7	18.5	14.0	43.7
07-906-96C	365	1150	2	88.83	9.50	0.56	0.33	0.78	0.38	79.6	18.9	14.2	44.1
07-911-96B	365	1800	3	89.06	10.18 ^e	0.51	0.33	-0.08	0.37	NES	17.5	14.7	44.2
07-829-96A	365	1800	2	88.44	9.82	0.44	0.28	1.02	0.25	85.5	15.7	16.1	45.3
07-828-96A	385	1800	2	88.60	10.36	0.29	0.19	0.56	0.13	83.8	13.7	18.6	47.2
07-905-96B	365	1800	1	89.02	10.09	0.27	0.16	0.46	0.14	NES	13.4	17.7	47.1

Note: Samples and hydrotreating conditions were provided by Sandia (Ref. 2).

- (a) SI equivalents are: 3.5 MPa = 500 psig, 7.9 MPa = 1150 psig, and 12.4 MPa = 1800 psig.
- (b) Aromatic protons = sum of condensed and uncondensed protons as given in Table 5.
- (c) Hydroaromatic protons = cyclic beta aliphatic protons as given in Table 5.
- (d) Paraffinic protons = sum of alkyl beta and gamma aliphatic protons as given in Table 5.
- (e) Value suspect
- (f) Microautoclave (MAC) test conditions were: 5.45 g solvent, 4.55 g Black Thunder Mine coal, 1500 psi (10.3 MPa) cold H₂ pressure, 840 °F (449 °C), 30 min, 45 mL nominal microautoclave volume, conversion to tetrahydrofuran solubles on a MAF basis (not SO₃-free MAF basis).

NES = Insufficient sample for test.

TABLE 5

**SAMPLE GENERATION CONDITIONS AND CONSOL PROTON DISTRIBUTIONS OF SAMPLES
FROM SANDIA HYDROTREATING TESTS**

Sample	Temp, °C	H ₂ Pres, psig (a)	WHSV, g feed/g cat-hr	Proton Distribution, %						
				Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
PFL-VSOH 227-90-16B (Feed)				16.8	7.5	13.7	9.9	11.5	27.4	13.3
07-913-96B	365	500	2	15.6	7.8	13.1	10.1	12.3	27.3	13.9
07-830-96A	345	1800	2	11.1	7.4	13.9	9.9	14.0	28.2	15.5
07-906-96C	365	1150	2	10.9	8.0	12.9	9.9	14.2	28.6	15.5
07-911-96B	365	1800	3	10.4	7.1	13.7	9.8	14.7	28.9	15.3
07-829-96A	365	1800	2	8.8	6.9	13.4	9.6	16.1	29.2	16.1
07-828-96A	385	1800	2	7.3	6.4	11.5	9.0	18.6	30.2	17.0
07-905-96B	365	1800	1	6.8	6.6	12.5	9.2	17.7	29.7	17.4

Note: Samples and hydrotreating conditions were provided by Sandia (Reference 2).

(a) SI equivalents are: 3.5 MPa = 500 psig, 7.9 MPa = 1150 psig, and 12.4 MPa = 1800 psig.

SECTION THREE

LDP ASSOCIATES

LDP ASSOCIATES

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609-586-2301

32 Albert E. Bonacci Dr.
Hamilton Square, N.J. 08690

July 31, 1997

Dr. Ed Givens
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433

Dear Ed:

Subject: QUARTERLY PROGRESS REPORT: APRIL-JUNE 1997

For the quarter ending June 30, 1997 the following subcontract services (UKRF-4-25582-92-75) were performed in support of the DOE Advanced Concepts Program (DE-AC22-91PC91040):

ALC-2 ANALYSIS

● Solids Inventory

The accumulation of solids in the bench unit during the early portion of the run was analyzed (see Table 1). It appears that solids continued to accumulate in the unit until the ninth day of operation (see Figure 1). The calculated total quantity of solids accumulated in the unit was two to three times more than expected.

Extraordinary accumulation of solids in the Continuous Vacuum Still Bottoms Receivers (O-18 & O-19) was suspected, but no appreciable amount of solids were recovered during flushing of HTI's unit.

● Effect of RPSOH Recycle

The effect of recycling Reduced Pressure Still Overhead (RPSOH) on the net make of RPSOH was quantified (see Table 2). As shown in Figure 2, the net RPSOH yield declined dramatically as the amount of RPSOH recycle increased. Although undesirable, recycle of RPSOH was often needed during the run to compensate for the inability to recycle heavier distillate and resid due to problems in the solids-separation units.

● H₂S Addition Rate

The difference between the targeted sulfur addition rate and the much higher

measured H₂S yields are shown in Table 3. The cause of this difference is suspected to be a higher than targeted H₂S addition rate to the first stage reactor.

● Catalyst Overlap

The calculated ratio's of recycle to fresh catalyst is shown in Table 4. Theoretically these ratio's should be the same as the ratio of recycle to fresh ash.

For molybdenum the recycle to fresh(R/F) ratio is approximately equal to the R/F ash ratio for all 4 run conditions.

The iron R/F ratio is approximately the same as the ash R/F ratio in condition #1

(iron catalyst addition), but significantly higher in conditions #2 through #4 (no iron catalyst added). Unless the iron concentration in the coal is higher than measured, a significant amount of non-coal iron was being recirculated.

The nickel R/F ratio was only measured in conditions #3 (nickel catalyst addition) and #4 (no nickel catalyst addition). There appears to be a significant amount of residual nickel being recycled in condition #4 which was 4 days after the feed of the nickel containing coal had been stopped.

SANDIA HYDROTREATING

Options for hydrotreating all or a part of an HTI Pressure Filter Liquid (PFL) were discussed with Fran Stohl of SANDIA. A proposed donor solvent type hydrotreating test program was received from SANDIA.

A review of SANDIA's proposed donor solvent type hydrotreating test program was conducted. Data from SANDIA's two earlier solvent hydrotreating test programs conducted during 1996 and the solvent hydrotreating work done during ALC-1 Condition #5 were analyzed and compared. The feedstocks used in the two SANDIA tests differed significantly in aromaticity although both were distilled pressure filter liquids (PFL's) supplied from HTI Run #PB-01. The properties of the feedstock for the proposed SANDIA test program will not be known until HTI distills the proposed PFL sample (Run #PB-03, Period 3) and it is analyzed by CONSOL. As in the first two SANDIA tests only a small amount of feedstock will be available for the hydrotreating test. Given the above limitations, it was suggested that an effort be made to find a more appropriate feedstock (i.e.highly aromatic and available in a large quantity). Such an alternate feedstock may be

available from HTI's tank L-814 after filtration and distillation (see Table 4 of ALC-2 Draft Report). Additional feedstock availability would allow the comparative testing of an alternate aromatics saturation catalyst to the Criterion C-411 catalyst previously used in both SANDIA tests and in ALC-1. In the hope that the feedstock quantity would be large enough to pursue this option, three catalyst vendors were requested to recommend an appropriate aromatics saturation catalyst for hydrotreating the distillate solvent feedstock. Several technical articles on aromatics saturation were reviewed to obtain background information on the types of catalysts being used in such applications.

MISCELLANEOUS

A presentation on the ALC-2 topics discussed above was made at the May Project Review meeting in Lexington.

Very truly yours,

Michael Peluso
LDP Associates

cc: F. Derbyshire @ CAER, R. Anderson @ CAER
R. Winschel @ CONSOL, T. Lee @ HTI, F. Stohl @ SANDIA

TABLE 1
CAER ADVANCED LIQUEFACTION CONCEPTS
ADDITIONAL PROBLEM AREAS IN RUN ALC-2
SOLIDS BUILDUP

- **During Startup Solids Concentration in CVSB Increased Much More Slowly than Anticipated**
- **Even After Four Days of Reasonably Steady Continuous Operation, Solids Leaving the Unit Were Less Than Solids Entering the Unit**
- **Where Were Solids Accumulating ?**
- **CVSB Bottoms Receivers Suspected; 2 Hour Holdup & No Recirculation**
- **No Appreciable Amount of Solids Recovered During Unit Flushing**

TABLE 2
CAER ADVANCED LIQUEFACTION CONCEPTS
ADDITIONAL PROBLEM AREAS IN RUN ALC-2
EFFECT OF RPSOH RECYCLE

- **Typical Production Rate = 4,000 to 6,000 Grams/Day (13% to 20% on MF Coal)**
- **Was Last Resort for Use as Recycle Solvent**
- **Between Periods 4 and 21 There Were Only 2 Days in Which RPSOH Wasn't
Used as Part of the Recycle Solvent**
- **The RPSOH Recycle Rate Was as High as 6,300 Grams/Day**
- **Net RPSOH Yield Was a Strong Function of the RPSOH Recycle Rate**

TABLE 3
CAER ADVANCED LIQUEFACTION CONCEPTS
ADDITIONAL PROBLEM AREAS IN RUN ALC-2
SULFUR ADDITION RATE

- Targeted H₂S Rate to First Stage Was 2.0 Wt.% Sulfur on MF Coal
- Targeted TNPS Rate to Second Stage Was 0.5 Wt.% Sulfur on MF Coal
- Results of Gas Analysis via GC Indicate Sulfur Addition Rates Were Much Higher Than Targeted:

<u>Period #</u>	<u>Wt.% MF Coal</u>	
	<u>Total H₂S Yield</u>	<u>First Stage H₂S Yield</u>
7	6.17	4.85
12	4.90	3.27
17	4.83	3.65
21	5.04	3.12

- HTI Alerted to Problem but no Resolution Yet

TABLE 4
CAER ADVANCED LIQUEFACTION CONCEPTS
ADDITIONAL PROBLEM AREAS IN RUN ALC-2
CATALYST OVERLAP

	<u>Condition#1</u> <u>Period #7</u>	<u>Condition#2</u> <u>Period #12</u>	<u>Condition#3</u> <u>Period #17</u>	<u>Condition#4</u> <u>Period #21</u>
Fresh Catalyst Add'n Rate, <u>PPM on MF Coal</u>				
• Moly	97	110	91	93
• Iron*	3,600	1,960	1,960	1,960
• Nickel**	4	4	55	4
Catalyst in Recycle Solvent, <u>PPM on MF Coal</u>				
• Moly	223	255	364	298
• Iron	8,780	7,090	10,380	8,640
• Nickel	NM	NM	135	75
<u>Recycle/Fresh Catalyst Ratio</u>				
• Moly	2.3	2.3	4.0	3.2
• Iron	2.4	3.6	5.3	4.4
• Nickel	---	---	2.5	19.0
<u>Recycle/Fresh Ash Ratio</u>	2.0	2.3	3.5	3.1

*Includes 1,960 ppm Iron Contained in MF Coal Before Impregnation

**Includes 4 ppm Nickel Contained in MF Coal Before Impregnation

ALC-2 SOLIDS PROFILE

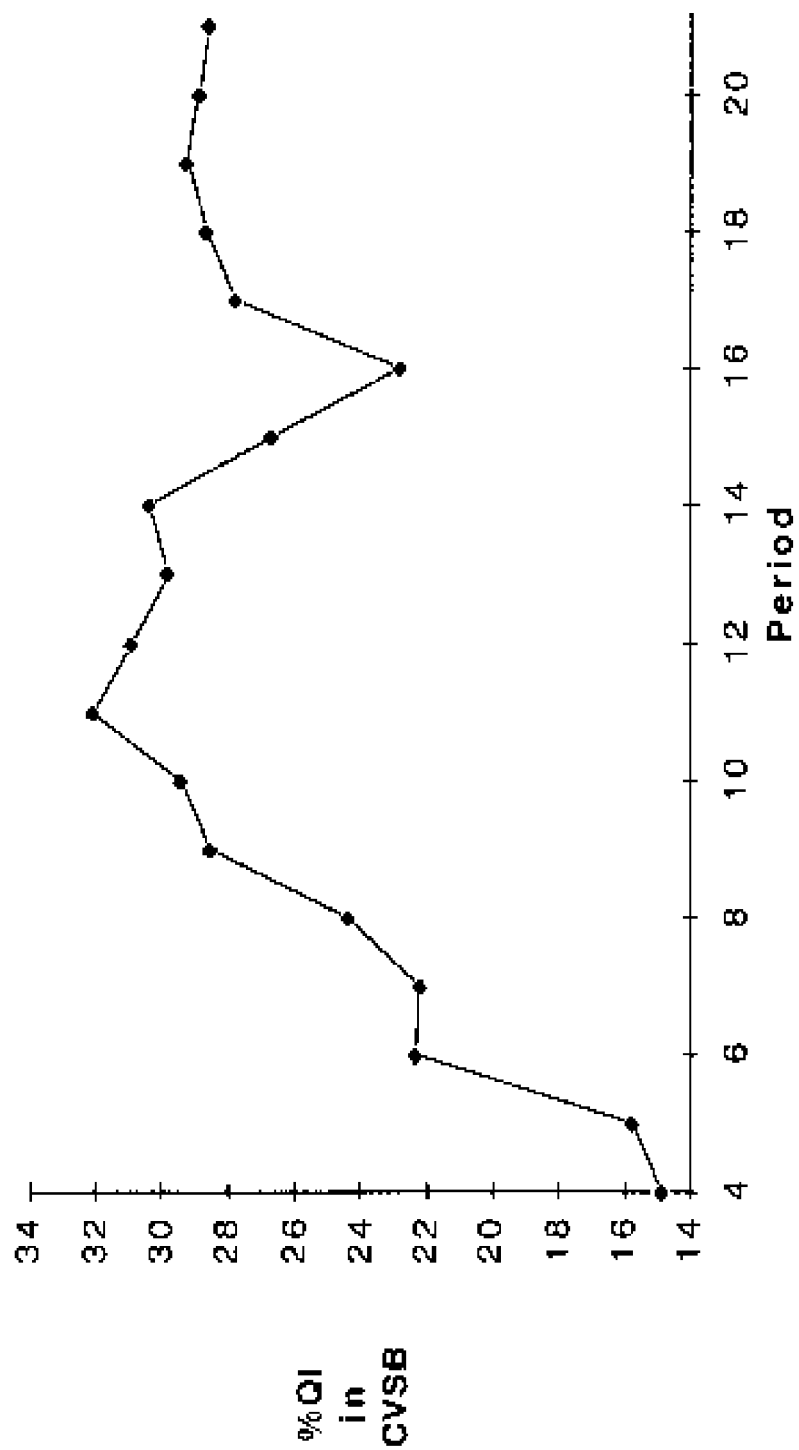


FIGURE 1

ALC-2 EFFECT OF RPSOH RECYCLE

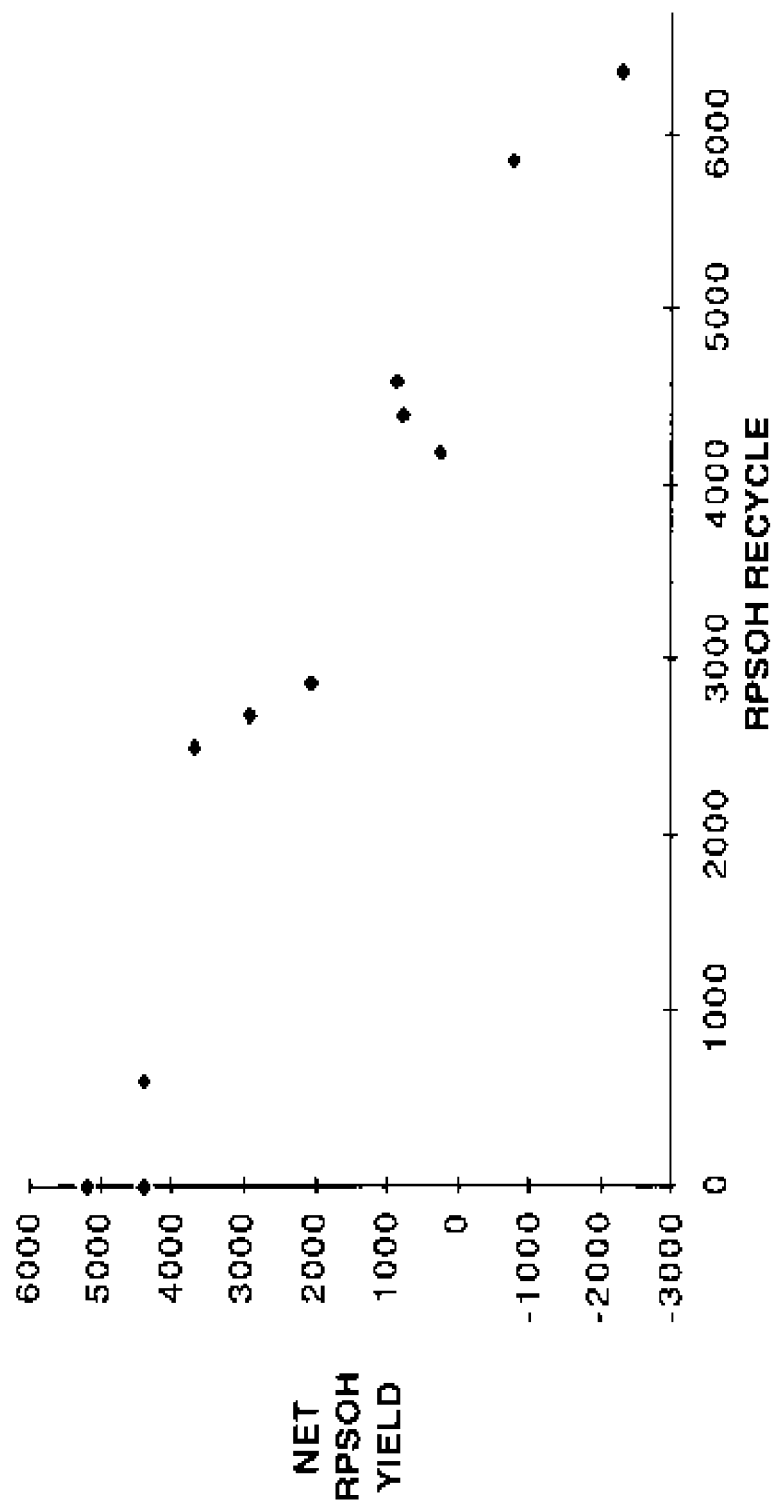


FIGURE 2

Abbreviations and Acronyms

AHM	Ammonium heptamolybdate
ALC	Advance liquefaction concepts
AN	Anhydrite
API	American Petroleum Institute
APTM	Ammonium polythiomolybdate
ASOH	Atmospheric still overhead
ASTM	American Society for Testing Materials
ATTM	Ammonium tetrathiomolybdate
BT	Black Thunder Mine
CC	Calcium carbonate
CAER	Center for Applied Energy Research
CAS	Continuous atmospheric still
CMSL	Run designation used by HTI
CST	Catalyst screening test
CVS	Continuous vacuum still
CVSOH	Continuous vacuum still overhead
CVSB	Continuous vacuum still bottoms
DAF	Dried and ash free
DW-HT	Dewaxed-hydrotreated
DW-HT-VSOH	Dewaxed hydrotreated vacuum still overhead
DW-VSOH	Dewaxed-vacuum still overhead
EDS	Energy Dispersive Spectroscopy
EO	Extracted oil
EOVSB	Extracted oil vacuum still bottoms
ES	Extracted filter cake
FBP	Final boiling point
FS	Ferrous sulfate
GC	Gas Chromatograph
HC	Hydrocarbon
HTI	Hydrocarbon Technologies, Inc.
HTU	Hydrotreater unit
IBP	Initial boiling point
IOM	Insoluble organic matter
J-1	Charge pump
J-2	Charge pump
K-1	First stage reactor
K-2	2nd-stage reactor
K-3	In-line hydrotreater
KA	Kaolinite
L-814	End-of-run makeup oil in Tank #4 from HTI's POC-02 run
MAF	Moisture and ash free
O-1	2nd-stage hot separator
O1-A	1st stage hot separator

O-2	2nd stage cold separator
O-2A	1st stage cold separator
O-3	2nd stage hot separator bottom flasher
OA	Oil agglomerated
P-2	Feed tank
PFC	Pressure filter cake
PFL	Pressure filter liquid
PMA	Phosphomolybdic acid
PY	Pyrrhotite
POC	Proof of concept
PPT	Precipitate
QI	Quinoline insolubles
QZ	Quartz
RPS	Reduced pressure still
RPSB	Reduced pressure still bottoms
RPSOH	Reduced pressure still overhead
SEM	Scanning electron microscopy
SIMDIS	Simulated distillation
SOH	Separator overhead
SSSY	Speculative steady-state yields
TBP	True boiling point
TE	Toluene extraction unit
TEO	Toluene extracted oil
TES	Toluene extracted solid
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TNPS	Ditertiarynonyl polysulfide
UK	University of Kentucky
VT	Vaterite
VSF	Vacuum still bottoms
VSOH	Vacuum still overhead